

**CHEMICAL
THEORY AND ARITHMETIC.**

**ELEMENTS
OF
CHEMICAL THEORY
AND
CHEMICAL ARITHMETIC.**

(Adapted for the Intermediate Science Course.)

In force from June 1924,

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1924.

Printed by S V Kamat, at Kamat Printing Press, Goverdhan Building,
Parekh Street, Bombay No. 4.

Published by R N Bhagvat, Chemical Laboratory,
St. Xavier's College, Bombay I.

PREFACE.

This little book is written solely with the object of supplying a want felt by the beginners in collecting full information on the matter of Chemical Theory or General Chemistry, as well as in selecting a separate book dealing with chemical calculations.

In this book I have tried to treat chemical theory and chemical arithmetic conjointly so that the student will get the treatment of the theory, immediately followed by the examples based upon it. The methods of working out the examples on the different theories are given in the typical examples.

I have always kept in mind the standard and have tried to make the subject matter as easy as possible. However to make the book a complete volume by itself, some three chapters are given which are not just exactly within the scope of the Intermediate Science students. I have adopted a separate kind of type for the subject matter which I think a little beyond the course but necessary to form a complete chapter by itself

This book is intended to be a very good substitute for the text-books by Smith or Holleman or Newth recommended by our University as supplements to that of James Walker. In the above text-books there are a good many points, though quite essential for our standard that are not there, especially as the books are written for the European standard where the student is already acquainted with a good many facts before he enters the science classes.

Some few appendices dealing with some useful points are given to facilitate the work of the students. Especially the University Examination questions given in appendix F will clearly show the utility of such a book and the importance the various examiners attach to this kind of subject matter. In short every attempt was made to make this book a very useful companion reader to the usual text-books wherein the Chemical Theory is distributed throughout the volumes to suit the individual subject matter.

I have taken full help of the various standard text-books, such as those by Holleman and Cooper, Newth, Senter, McPherson, Alex-Smith, Hilditch, Coward and Perkin, Sears, Bauser, Hale, and etc. I am indebted to the above gentlemen and specially so to Rev Fr. J. F. Caius the Director of our laboratory for lending me his private note-book and allowing me the use of it in casting up these chapters.

I sincerely thank Prof S. K Chhapgar B.Sc. and also Mr. J. B. Sane B.Sc. for going through the manuscript.

The present volume is printed on the best Indian paper available, here in the Bombay market

St Xavier's College,

16th June 1924.

R N. BHAGVAT.

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Bombay University
Intermediate Science Course.

(Revised. In force from June 1924.)

General Chemistry.

The character of physical and chemical changes including solution, distillation, crystallization, dissociation, combustion, precipitation, neutralization, electrolysis, the conditions which influence and determine them and the attendant phenomena. Catalysis.

Acids and bases.

Oxides, their formation and classification.

The formation and decomposition of salts.

Oxidation and reduction.

The general laws of gases. Avogadro's hypothesis.

Molecular weights. Experimental determination of the density of gases and of vapours. Atomic hypothesis. Experimental determination of atomic weights. Symbols, formulæ, equations and chemical calculations. The simple gas equation.

Mass action.

Water of crystallization, efflorescence, deliquescence.

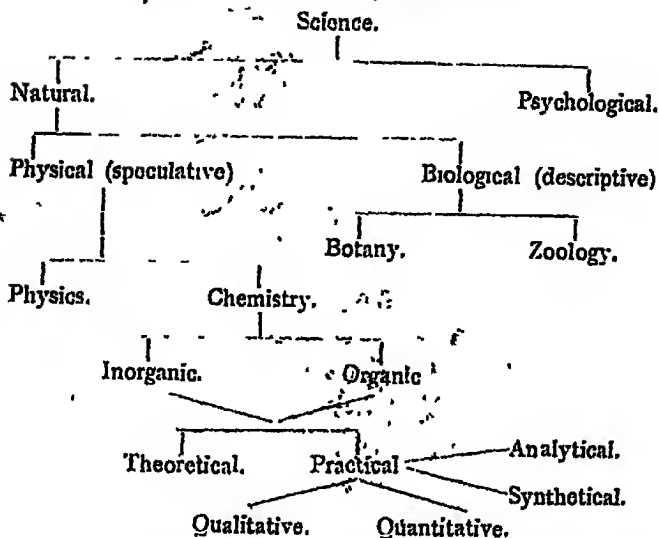
ELEMENTS OF CHEMICAL THEORY & CHEMICAL ARITHMETIC.

CHAPTER I.

Introductory.

Chemistry as an *art* was practised thousands of years ago, before the Christian Era, but as a science it dates no further back than the middle of the seventh century.

"As a science chemistry is essentially a thing of the present, or rather of the present and the future. Its progress has been so rapid, and often so sensational, and it has so frequently revolutionised industry and trade or modified civilization by the introduction of new and widely used comforts that its votaries are apt to forget that it has a past. They forget that many chemical facts, products and processes have been known from a period considerably earlier than any of which we have a historic record. As a true science, indeed, chemistry is only between one or two hundred years old just as astronomy is less than three hundred years, but like astronomy, it has been known and practised as an art continuously since prehistoric times. Just as astronomy had its false philosophy, and was by astrologers associated with superstition, so the great philosophers taught false doctrines concerning chemistry, and alchemy was associated with superstition in the hands of magicians of the Black-Art and transmuters of the metals".



Science is called universal knowledge derived from particular facts, and art is the application of that universal knowledge to particular facts.

In general usage the modern term Science (Scientia from Scire=to learn, to know) has come to mean an ordered knowledge of the phenomena or appearances of Nature, and of the connections or relations which have been discovered between them.

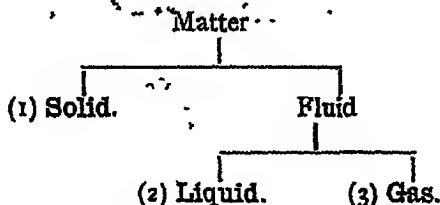
1. **Psychological Science.** (Psyche=soul) is concerned with the phenomenon of the mind and the influences affecting it, primarily of course the mind of man.
2. **Natural Science** :—Every thing that exists or every thing that which itself or its effects can be felt, is Nature or Universe, and hence its knowledge is natural science. It is divided into two branches (1) Descriptive, and (2) Speculative.

3. **Biological Science** (*Bios*=life, *logos*=discourse) treats of living things and of those special problems of matter and energy to which their life gives rise.
4. **Physical Science** (*A. physis*=*L. Natura*) is that part of science which deals with matter and energy without reference to life.

Physical science is divided into *physics* and *chemistry*. Physics deals with temporary, and chemistry with permanent or lasting changes in matter.

"Matter is anything that exists or whose existence can be recognised by the help of our five senses" (Sight, taste, touch, smell and sound), or anything that occupies space and has weight is called matter. "Anything possessing extension and impenetrability".

It may be in either of the three forms, or states of aggregation.



These can be easily distinguished from one another by their characteristic properties. The chief ones are :—

A solid substance retains its shape unless or otherwise acted upon by some external force. The amount of force required depending upon the nature of the solid—soft or hard—as well as on its original shape. Thus a piece of lead is more easily bent than a similar piece of iron; and a strip of tinfoil more easily than a thicker strip of sheet tin. A solid body has the property of regaining its original shape provided the force applied is not too great; and thus it is said to be elastic as regards shape. The volume of a solid is almost incompressible at constant temperature.

The shape of a liquid, on the other hand, is very easily altered and assumes the shape of the vessel in which it is put as for example when water is poured from one vessel into another. Liquids are just as solids almost incompressible but just slightly more than the solids.

The shape of a gas is not only more alterable than that of a liquid but when placed in any vessel, the gas has the property of filling completely and hence assuming the shape of the container. Again the volume of a gas is very easily affected by pressure unless and otherwise it is already too high. Thus to define the three states of matter —

A Solid is that whose particles have greatest cohesion and hence a solid has a definite size and shape.

A Liquid is that which though has a definite size has no definite shape as the cohesion between its particles is not much.

A Gas is that where the particles have not only no cohesion but on the contrary appear to have repulsion though really it is not so and thus have no definite size and no definite shape

Coming again back to the history, definition and origin of chemistry we have to say that "Chemistry is that science which by means of experiments tells us of the composition and properties of all the bodies composing the Universe" or

"Chemistry is that branch of natural science which deals with the intimate composition of bodies" or

"Chemistry treats of the composition and molecular structure of substances, of their properties in relation to their composition and molecular structure, of changes in their composition, and of the effects attending such changes. Physics treats of the properties of substances without relation to their composition, and of changes in state that do not involve changes in composition."

The Indian equivalent for Chemistry, 'रसायनशास्त्र', 'रसायन शास्त्र', Rasayana Shastra, [रस = Juice, and आयन, आयन = Way.] in older works means science of medicine, preventing old age and prolonging life. Later on it was applied to the employment of mercury and other metals in medicine. Incidentally then it came to mean also alchemy, and now it means even chemistry proper.

The English word chemistry comes from the word alchemy which in turn is supposed to be from Khem or Chemia = Egypt, the land of dark coloured soil. Hence an art developed in that land (dark coloured) is Chemia. Then the adjective of the soil was somehow or other transferred to the art and thus it became a 'Black art'. It therefore was a black art either from the colour of the soil or from the fact that it was preserved very guardedly (especially by priests) as it used to give many miraculous results. Instead of black some will have it as a 'secret art', a science not to be divulged to the populace but treasured up as a religious secret. 'The priests were adepts in chemical art, and chemical laboratories were occasionally attached to temples.

The origin of the science of chemistry must, therefore, be sought in the art of alchemy. The alchemists were mistaken in many of their ideas, and engaged themselves in a search for what was by them unattainable, yet in the course of their labours they gained much definite information regarding substances, devised and performed many apparatus and chemical operations, thus giving a large collection of facts for the future workers to base their theories on them.

Chemistry as an art can be traced even to the Vedic period (2000 to 700 B. C.). Later on we find chemistry developed only as regards medicine and surgery.

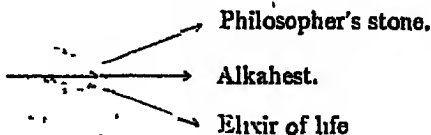
The alchemists were after finding out three things, (1), Philosopher's Stone (परिस्), (2) Alkahest (that which dissolves all), and (3) Elixir of life (अमृत).

The gradual development of the chemical science may be considered roughly to have the following order :—

Medical (& surgical)

↓
Technical (preparing medicines)

↓
Alchemical

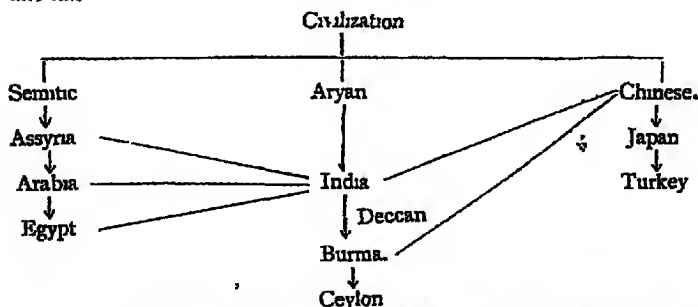


↓
Chemistry proper

चरक, चरक (200 to 300 B. C) Charaka, a book on medicine, and सुश्रुत, सुश्रुत Sushruta (800 A. D.), a book on surgery are supposed to be containing bold attempts in chemical art. Surgery died on account of the Buddhistic influence.

The use of the expression 'Chemist' to indicate a 'druggist' reminds us of another branch of alchemy, the art of making drugs as opposed to the expression chemist to indicate an individual adept in chemical philosophy.

Ancient Civilization in general belonged to three chief schools having mutual influence on one another at different periods It is something like this —



The following are the chief subjects which were the speciality of the different countries

- Assyria → Navigation
- Egypt → Stone work and Wood work
- India → Cotton and Metals.
- China → Porcelain and Printing

Hypothesis - Theory - Law - Fact.

It is a common belief that the aim and object of science is to explain things. As a rule the so-called explanations of science do not usually get much beyond describing the observed facts or phenomena. Science may explain a phenomenon by describing how one event is determined by an antecedent event -*cause*- , and how one particular set of conditions -the cause or causes- can give rise to another set of conditions -events-. But owing to the limitations of man's understanding we are far from comprehending the true relations and the true causes of natural phenomena.

Chemistry -an experimental science- is based on facts, established by experiment. A mere collection of facts, however, does not constitute a science. When a certain number of facts have been established the chemist proceeds to reason from analogy as to the behaviour of systems under conditions which have not yet been investigated. From the results of these investigations he concludes from analogy the nature of the behaviour of the above and proceeds to generalize, and the short statement of the conclusion arrived is termed a 'generalization' or Law. It will be evident that a law is not of the nature of an absolute certainty. It comprises the facts experimentally established, but also enables us to foretell a great many things which have not been, but which if necessary could be investigated -experimentally-. The greater the number of cases in which a law has been found to hold, the greater is the confidence in its validity, until finally a law may attain practically the same standing as a statement of fact.

Natural laws can be discovered in two ways :—(1) by correlating a number of experimental facts, or (2) by a speculative method on the basis of a certain hypothesis as to the

nature of the phenomena in question. As referred to already, owing to limitations of man's understanding, we are compelled to build an imaginary model showing how a given set of conditions—hypothesis—can produce a (certain effect) particular event. A phenomenon is then explained by showing that it would be bound to occur by the operation of the set of conditions postulated by the hypothesis, and consequently hypotheses are eventually guesses at truth.

A hypothesis may therefore be defined as a mental picture (of the mechanical model which, if real, would act in the same manner) of an unknown or largely unknown, state of affairs, in terms of something which is better known. From the statement of the hypothesis conclusions can be formed, some of which can be tested by experiments. If the latter really lead to expected results, the hypothesis gains in probability. If it is subsequently found to explain and link together a whole series of phenomena, it becomes a Theory, and so the process of constructing a mental picture of such a kind is called 'forming a theory'.

There does not appear to be any fundamental distinction in the use of the terms 'hypothesis' and 'theory'. A theory may be defined as hypothesis, many of the deductions from which have been confirmed by experiments, and which admits of the convenient representation of a large number of experimental facts.

An hypothesis contains a speculative term, an assumption which goes *beyond* the observed facts; while a law is a generalization which does not extend beyond the observed facts. A law is thus limited by the facts it describes, when an hypothesis has been so extended that it has a wide and comprehensive scope, the hypothesis becomes a theory. Like

the hypothesis, a theory usually contains an "unproved" assumption—e. g. the kinetic theory, the atomic theory.

The meaning of laws in Science. In scientific language some fact which is the *invariable rule* is called a 'Law', and you must distinguish clearly, at the outset, between the word 'Law' used in the scientific sense as just explained, and the same used in ordinary language to describe an artificial rule, such as laws of Indian Government. These scientific laws offer no explanations of the facts which they state, nor do they place any restrictions upon nature, which compels obedience, as the laws enacted by a legislature bind a society. They are in short, simply concise statements of what might be called "the habits" of nature as observed in experiment, and state that something fact which under the requisite conditions, always happens without exception. ✓

CHAPTER II.

Constitution of Matter.

It is but quite natural that when we begin to look round about us and begin to think about all the phenomena and the occurrences that are taking place every day, the first thing that strikes us is about the why and wherefore of everything. This natural curiosity further leads us to the examination of the things that are taking part in these various phenomena. This curiosity and the consequent experiments reveal to us that the variety of forms which matter assumes in all the wonderful transformations of nature is practically infinite, and these can be classified in a great many ways according to the object in view. The chemists are chiefly concerned in the composition of substances and in their chemical energy, together with the changes that take place in both of these

Everything around us is said to be composed of 'matter'. A clear and satisfactory definition of such a fundamental conception as *matter* cannot be given, but for our present purpose we may regard :

Matter as anything possessing Extension and Impenetrability or which occupies space and has weight, or that which can be felt by our five senses, in short matter is that which exists. Any definite but limited portion of matter such as a piece of sulphur or a piece of granite or a lead pencil is termed a body or a thing. Bodies differ, however, in com-

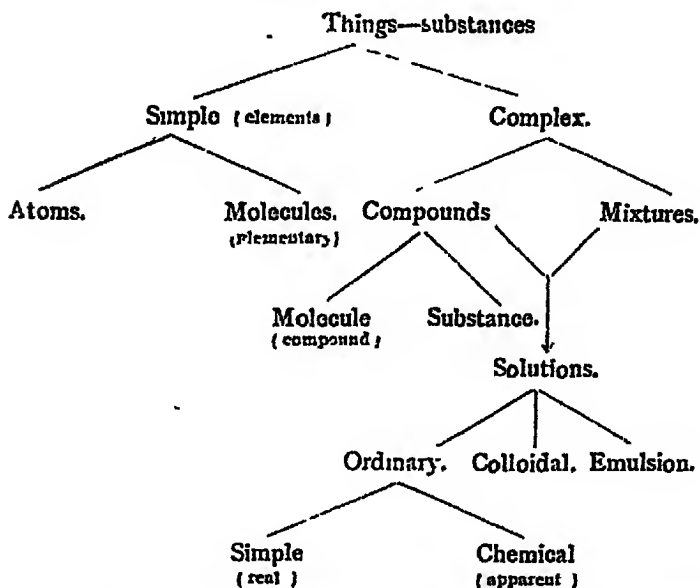
plexity. The material of which the piece of sulphur is made up, is homogeneous to the naked eye, and even under the microscope, whereas in things like granite three different constituents can be readily distinguished—a white crystalline part termed quartz; a grey portion, feldspar; and the third nearly colourless lustrous scales, mica—. Each of these three components is in itself uniform or homogeneous to the naked eye. Such homogeneous materials which are definite kinds of matter are termed substances, whilst sulphur is made up of a single substance, granite is made up of three substances, each of which is characterised by its special properties.

The important distinction between bodies and substances should be carefully noted. Pins, chains, hammers, screws and nails are different bodies, but all of them may be composed of the same substance, steel.

Having seen the differentiation between matter, substance and body, the next things naturally to be considered are the products of the various analyses. Experiments clearly show that a good many substances can be split up into somethings simpler than the original ones. Thus if we take water or red oxide of mercury, we know that any of these two apparently simple bodies can be split up at least into two each, provided sufficient temperature is allowed. But if we take a handful of sand from the sea-shore or a piece of a brick, we see with our naked eyes that there are different kinds of particles. Not only this but further these particles are so different from one another that we can separate some shining material, some dull black material, some red material and so on.

Thus we see that all the materials around us are neither simple things alone nor things made up of different things put together alone; but we come across both types, and the

complex ones can be separated into simpler ones either by easy means or some powerful agents. Hence :



* The results of various analyses show that most substances can be split up into something simpler but there are about eighty bodies which cannot be decomposed nor can be formed by the union of the other bodies. As yet no chemist has separated from oxygen anything but oxygen, from sulphur anything but sulphur, nor from mercury but mercury. These simple substances are therefore called elements (elementum = element). Element is therefore a conventional term employed to represent the limit of the present day methods of analysis or decomposition.

Thus an element is a body which cannot be split up into anything simpler by (human) means at our disposal. It is also called a 'chemical primary.'

In course of time it came to be known that elements, besides being undecomposed have other properties in common —

1. All elements in the solid state have an atomic heat (atomic weight \times specific heat) approximately equal to 6.4.
2. They can be assigned a fixed place in the periodic table.
3. Every element has a spectrum characteristic of its own, and quite different from any other element.

Hence, now-a-days, a body incapable of any further decomposition into still simpler bodies by any means at our disposal, having an atomic heat equal to 6.4, fitting well in the periodic table and having a characteristic spectrum is called an element.

The number of elements is steadily increasing either due to the discovery of quite new ones being discovered that had escaped detection or isolation so far, and secondly to the decomposition of a substance so far considered as an element into still simpler bodies. In short the differentiation as it stands is only a question of advance of knowledge, both with regard to apparatus and fundamental theories and manipulation thereof. Thus we see in all the countries to start with, they had only a few elements, viz. earth, water, fire, wind and sometimes the sky. But as the information about things around went on increasing the number of elements also increased, and for the present as already said we have about eighty on the list.

So far as we can judge the quantities of the various elements occurring in nature are very unequal. It is found that 20 of the elements are found to constitute 99.5 per cent of the earth's crust so far reached, and the other 60 together make up

the remaining 0.5 per cent. Some of the elements are of such rare occurrence that only a few grams have been isolated.

				average quantities.
Oxygen	49.78 %
Silicon	26.08 "
Aluminium	7.34 "
Iron	4.11 "
Calcium	3.19 "
Magnesium	2.24 "
Sodium	2.33 "
Potassium	2.28 "
Hydrogen	0.95 "
Carbon	0.19 "
Chlorine	0.21 "

and so on.

Coming to complex bodies we find that some of them are made in such a way that the constituents cannot be separated by simple and easy means. Still further when the constituents are examined it is found that the properties of the constituents and the original body have no agreement whatsoever. Nay, as a rule they are absolutely different. Take for instance the above quoted case of water or red oxide of mercury. We know that oxygen is a gas and also colourless, and mercury is a liquid and silvery white in colour while the original substance was not only solid but red in colour. Similar is the case with water. This is a liquid body often used to quench fire and people diving in it suffer from suffocation, but the two gases got from it show different properties from their parent substance. Hydrogen burns and oxygen supports respiration.

When compact combinations of the above types are there, then these are called compounds.

These compact combinations follow certain fixed rules and as the result of this, it is noticed that the nature of the compound is of a very uniform character i. e., homogeneous

(every smallest portion is identical in composition with every other portion); and during formation the constituents combine in a fixed proportion and the excess of one or the other is left out, and during combination either heat is given out or taken in. Thus :—

✓ A compound is a homogeneous body composed of at least two different materials; the components of which combine in a fixed ratio, and the combination is followed by a change in properties and chemical (thermal) energy.

A compound is made up of two or more elements (even two or more compounds) of different kinds and hence their number is practically infinite.

✓ When the combinations are not quite compact like the above mentioned sand or graphite pieces, then these types of formations are called mixtures.

As the combination in a mixture is of a loose kind the different components need not and are not in any fixed proportions, and secondly as their combination is of simple association and not actual blending, the constituents still maintain their own self, and as such the result is that the properties of a mixture are the properties that can result from the algebraic sum of these properties. Thus :

✓ A mixture is a heterogeneous body the composition of which can be varied at will and the mixing up of the components does neither result in any thermal change nor change of properties

A compound is formed as a result of a reaction by which two bodies either elementary or compound unite by addition of their masses so as to form a new body.

The products of the chemical combinations contain less energy than the materials from which they are formed, the difference being disposed off in the form of heat.

A *compound* is to be distinguished from a *mechanical mixture*.

Chemical compound.

1. In a compound formed of several bodies, every single body individually loses the whole or part of its properties.
2. The compound itself possesses new properties different from those of the component bodies.
3. Bodies can never be compounded or combined in all, but always in definite proportions nor is the number of the component bodies unlimited.
4. The bodies forming a compound are never mechanically separable.
5. Compounds are homogeneous bodies.
6. Production of a compound results in change of thermal energy.

Mechanical mixture

1. In a mixture of several bodies every single one of the bodies individually preserves its properties, which are always to be recognised in the mixture though in some way kept down by those of the other bodies of the mixture.
2. The mixture itself does not possess new properties different from those of the mixed bodies.
3. Bodies can often be mixed in all proportions and in an unlimited number
4. The bodies forming a mixture are mechanically separable.
5. Mixtures are heterogeneous bodies.
6. No change in heat when mixture is formed.

Having classified the variety of forms which matter assumes, into three groups namely elements, compounds and mixtures, still we are confronted with certain substances which

cannot be definitely classed into one or the other. In many cases the two types, compounds and mixtures, approach so nearly each other that it is almost impossible to distinguish between them. Take for example alcohol and water. These can be mixed in all proportions, and they form a homogeneous body. Again when copper and zinc are melted together they form the yellow metal brass, which in properties is quite different from either, yet has no fixed percentage composition. A perfectly definite compound like water may be regarded as standing at one end of a series, with an undoubted mixture like granite at the other. There is every gradation between these two extremes, and in the middle of the series the one type changes by almost imperceptible stages into the other. In the majority of the cases, the distinction is easily made and affords a useful basis of classification.

Intermediate between compounds and mixtures, as already seen, there is a class of bodies which are classified as solutions, the most familiar types of which are solutions of solids in liquids.

They differ most noticeably from mixtures, in that they are perfectly of even character throughout, which fact is usually expressed by saying that they are homogeneous.

They differ from definite chemical compounds in that their compositions can be varied within wide limits, and that too gradually. Therefore :

✓ "A solution is a body of homogeneous character whose composition can be varied continuously between certain wide limits "

So far we have only considered the possibility of dividing matter into simple substances. At this stage naturally a question arises as to whether the divisions and subdivisions go so far and no further or they can still be continued further down. This idea of continuous divisions is not a new one but on the contrary a very old one. More than two thousand

years ago both the Hindu and Greek philosophers or better sages had propounded the atomic theory of the constitution of matter. The argument was this that suppose we imagine, that we can go on dividing and subdividing matter, and carry on the process till we come to infinitesimal fractions thereof, where are we stop? And stop we must because we must reach a limit of smallness (in size) of matter which can not be any more split up into parts. There must be a limit beyond which we cannot go. The ancient philosophers were thus led to suppose that matter must be made up of ultimate indivisible particles *i. e.* atoms (*a*=not; *temno*=to cut). Take for instance the gas, oxygen. If we start with say 1,000 c. c of it we may divide it into two parts *i. e.* 500 c. c each. This further into two parts 250 c. c each and so on. Ultimately we will be confronted with this state of division where we reach our limits. In this case what we have seen is that the different parts are made up of the same material oxygen, and no other thing but oxygen is got in this subdivision.

These philosophical high soaring imaginations of course lead us to a final limit *i. e.* to atoms, but now comes the difficulty of putting these imaginary conceptions into practical tests and to see whether such a state of things really exists and atoms have an existence for themselves. While verifying these ideas it is found that though atoms may be existing—and they are existing—still these atoms have no independent existence for themselves singly and alone; *i. e.* one atom of an element cannot exist by itself. It must either combine with one or more atoms of the same element or other elements, for having an independent and separate existence. These combinations of different atoms—of the same element or of different elements—are called on account of their very nature, of being collections or masses of atoms, molecules (molecules a diminutive of Moles=mass). Thus we can see that we can imagine freely existing particles *i. e.* molecules, both in an element or in a compound, but with regard to atoms as these are ultimate indivisible particles, we can not imagine of getting these particles while keeping the nature of the compound intact. If we have to reach the ultimate indivisible state we must perforce break the

compound, as by its very nature it is made up of at least two elements. From the above explanations we can now define :

✓ An atom is the smallest particle of matter which can take part in a chemical change ;

or

Atoms are the smallest supposed indivisible particles of an element, which are incapable of separate existence ;

or

The unit quantity for chemical combination of each element, and further

✓ A molecule is the smallest particle of matter capable of independent existence ;

or

✓ The smallest group of atoms of any substance whether an element or a compound which is believed as capable of a separate existence is called a molecule

or

Molecule is the smallest unit either of a compound or of an element, which taken in large aggregations, makes up the bodies we deal with and into which substances can be divided without chemical decomposition.

or

The smallest weight of matter in which the original properties of matter are retained.....In the strictest sense *matter is not continuous.*

The atoms of any element or the molecules of any particular substance are alike in nature, structure and mass.

Atoms are by no means solid masses but far from it. Each atom is probably composed of thousands of tiny specks of negatively electrified bodies which fly about in astronomical orbits.

The mass of a body is explained by the electronic theory of matter as an effect of electricity in motion. If it is so, it can be shown that the mass of a body must increase with the velocity. Actual experiment by Kaufmann showed that this is the case.

These particles of which molecules are composed are termed atoms and the force which holds them together is called chemical affinity or chemical attraction. The chemical forces exceed that of the gravitational forces which the bodies exert. The chemical forces are selective while the gravitational are not selective. "The atoms in fact are dreadful snobs and are most particular with whom they associate"

The Atomic Theory.

"Dalton -1808- took as his basis the old atomic theory, but added something more to it. He took for granted that an element is made up of ultimately indivisible particles or atoms, and at the same time assigned to each atom of an element a fixed and invariable weight. He also assumed that when a compound is formed of two or more elements, it is by the juxtaposition of the individual atoms of these elements. From this the fully developed theory is as follows—

All substances, whether elements or compounds, consist of small particles, indivisible or atleast not capable of division by any means which we have at our disposal. These particles are named atoms. All the atoms composing any one element are precisely similar and have the same weight but differ to a recognisable degree from the atoms of all other elements. Chemical combination of two elements consists in the union of a small fixed number of atoms of one element with a small fixed number of atoms of the other to form each and every part of the compound. The resulting body differs from its constituents as a general rule, and in this, as well as in the fact that combination takes place in definite proportions, chemical combination differs from mechanical attraction —mixture—.

When two elements form more than one compound, the compounds as has been remarked, contain different numbers of atoms of the constituent elements. Thus we may have $A+B$; $A+2B$; $2A+B$; $2A+3B$; etc

All the atoms of a given element are alike in regard to their weight and other properties, but the atoms of any one

element differ from those of every other element. Thus all atoms of hydrogen are supposed to be of equal weight, and in other way similar, and so are all the atoms of oxygen; but hydrogen atoms are supposed to differ more or less from oxygen atoms in all respects, except that both possess the fundamental property of indestructibility.

If we compare the atomic theory with the laws of combination we see that they are concordant. For example, matter made up of a finite number of indestructible and uncreatable particles would as a whole be indestructible and uncreatable. Again if the atomic theory be true, chemical combination could only take place in accordance with the laws of Constants and Multiples. Let us suppose for example, that atoms of oxygen are sixteen times as heavy as atoms of hydrogen. Then since combination can only take place, between definite numbers of atoms, and since these atoms have fixed weights, water cannot exhibit any slight variations in its composition. A given particle of water might contain two atoms of hydrogen weighing 2, with one atom of oxygen weighing 16, or 1 part of hydrogen to every 8 parts of oxygen, but since fractions of atoms cannot exist, it could not contain slightly different proportions, such as 8.2 parts of oxygen to 1 of hydrogen. It is conceivable, of course, that one particle of water might consist of 16 parts of oxygen with 2 of hydrogen, and another of 16 parts of the former for 1 of the latter, for one atom of oxygen 16, might combine with one of hydrogen; but we find such differences of property like those we have met with in the case of the oxides of hydrogen: water and hydrogen peroxide.

Thus to summarize:—

1. Matter is composed of minute particles incapable of further division called atoms.
2. Atoms of one element are alike in weight and of different elements are different in weight.
3. A compound is formed by the union of atoms of different elements.

- 4 A particular compound is formed by the union of atoms of the same elements in the same proportions.
5. The combining weights of elements are the combining weights of atoms.

If we compare the atomic theory with the laws of combination we see that they are concordant.

Clause (1) explains the indestructibility of matter and hence the conservation of mass.

Clause (2) explains the difference in properties exhibited by different elements.

The difference in properties is due to difference in weights. (According to Atomists before Dalton, the difference in properties was attributed to difference in form and size)

Clause (3) explains the difference between elements and compounds.

Clauses (1) and (3) account for the law of multiple proportions. For example suppose there are two elements A and B, then 1 atom of A can only unite with 1 atom of B or 2 or 3 atoms of B. It cannot unite with a fractional part of the atom of B, for then the atom would be destructible in contradiction to clause (1). If such be the case the various masses of B which unite with a fixed mass of A, bear a simple ratio which is the law of multiple proportions.

Clause (4) accounts for the law of definite proportions.

Clause (5) accounts for the law of combining weights.

Do chemists really believe that the atomic theory is true?

The answer is that they do not know.

The important question about this, and all similar theories, is not—

Do they give us true and complete picture of the subjects they deal with, but.....Has each a sufficient element of truth in it to be useful?

A theory like the atomic theory is or ought to be, a kind of tool, something to be used as long as we can do good with its aid, but which must be discarded when it ceases to be efficient for its purpose. So long as a theory is fruitful in promoting discovery, and so long as it helps us to grasp the subject to which it relates, it may be retained and used, but we must be ever on the watch to improve it, and ready to set something better in its place at the first opportunity.

Although the theory accounts for the laws of chemical combinations there are certain defects in Dalton's Atomic Theory. Although matter has concrete existence, its constituent particle, atom, has hypothetical existence. The idea of atom is the outcome of pure imagination; secondly the theory lacks a standard for fixing the atomic weights and lastly although the theory states that atom is indestructible, the experimental evidence is contradictory. The passage of electricity through rarified gases shows that atom is destructible and is composed of negatively charged particles aggregated together.

The last is the serious objection to the theory. In spite of this the theory is retained because it serves useful purpose and facilitates our work in the study of other branches of chemistry.

1. It explains the laws of chemical combination.
2. In organic chemistry the idea of an atom is indispensable. The organic compounds are classified according to their structural formulæ and great confusion will be introduced by discarding the idea of an atom and hence the atomic theory.
3. Lastly in conjunction with kinetic theory of gases it explains other phenomena.

The justification for the position given to the atomic theory by chemists is this, that it has done splendid service in the past, and seems likely to be useful in the future. It should be added that since the atomic theory was first

expounded by Dalton in 1808, it has undergone some modifications and expansions, and that further changes are not likely to become necessary as our knowledge progresses.

"Like any good theory, the atomic theory is useful chiefly in affording a concrete image of the mechanics of the topic it covers—in this case chemical action and in suggesting profitable investigation. It does not make a great deal of difference whether or not such things as atoms actually exist, and nothing short of seeing them will ever conclusively settle the question. The main question is: Does the mechanical conceptions correspond to all known facts? If not what are the exceptions, so that we may keep them in mind and not be misled by the theory? It may be said that the theory has been found to be in remarkable accord with all we know about matter, that it has been the incentive to a vast amount of profitable work, and that the number of facts not in accord with the theory is not large. When properly regarded it is a very helpful conception."

Hence therefore if the question is asked—why do we not discard the theory in view of its defects? The answer is this that the atomic theory is a good servant whose services cannot be dispensed with without causing inconvenience. ✓

CHAPTER. III.

Conditions for a Chemical Reaction.

Before we enter into the conditions we must arrive at the meaning of the term reaction.

Reaction: Action owing to which bodies modify their constitution, so as to cease being what they were, and gives rise to the formation of one or more new substances.

All reactions are controlled chiefly by the following : (1) Affinity, (2) Suitable state, and (3) Temperature.

I. Chemical affinity: There must exist what is called chemical affinity between the substances which are to or to be combined.

Chemical affinity is that selective peculiar force (like gravity) by means of which certain elements, or groups of elements with dissimilar properties attach themselves to one another, to form new substances.

This word affinity is quite different from the ordinary word. There it means attraction due to similarity of properties, or ideas, or relations or connections. Here it exists between substances which are of *different nature* and *increases with increase of dissimilarity* : e. g. Oxygen and hydrogen combine, but chlorine and hydrogen do so more easily because of the disagreement in the properties, while fluorine and oxygen do not combine at all.

"Chemical affinity, to put more in a metaphorical way, would mean 'Love' if love be the desire for marriage".

Affinity may be defined also as "the atomic force which tends to bring atoms together to form molecules".

Its nature is unknown.

II. **Suitable state:** In order that substances may combine they must be in a condition so that the affinity can act, and for that chiefly two conditions are essential: (1) Close contact, and (2) Suitable state.

(α) **Close contact:** Substances if they are to react must be sufficiently near one another.

If the substances though in touch are in large pieces they would not react, because the surface of contact would not be sufficient for the rapid chemical combination. *e. g.* Sulphur, coal and nitre, if in large lumps or pieces, would not form gunpowder.

Similarly sugar and chlorate of potash merely put together would not start any reaction. The sugar would not burn because the oxygen is apart from it, and is in combination with potassium chloride. But if a drop of sulphuric acid is put on the mixture, oxygen gets developed and is now sufficiently close to combine.

(β) **Suitable state:** It does not always suffice to have the substances in close touch or contact with one another. There are some substances that do not combine unless and otherwise they are in a particular physical condition. This is more or less a modification of the (α) case.

Powdered soda-bicarbonate and powdered tartaric acid will not at all react even if they are thoroughly mixed together in a mortar. But if one or both are in a dissolved condition, then they interact immediately and a lively effervescence comes out.

III. **Temperature:** A certain temperature is always necessary for each and every reaction otherwise called 'temperature of reaction' just as the ignition point for substances to start burning. Now there are certain reactions which unlike many common

reactions absorb heat or are endothermic, and when such a reaction is taking place the heat being absorbed, the temperature falls down and the reaction is brought to a stand still. So two points must be observed (1) a particular (height) temperature and further more (2) continuation of that temperature.

(α) A certain temperature is necessary.

When a chemical combination takes place a certain temperature is necessary for it. This temperature varies with the difference in the nature of the substances combining. If the necessary pitch in the temperature is not reached then the combination does not take place, and the elements remain unattacked. *e. g.* Nitrogen and oxygen do not combine under ordinary conditions but if the temperature is raised then they combine.

(β) The temperature must be maintained throughout.

As already said there are some reactions that are endothermic, and in such cases the temperature *i. e.* heat is absorbed and then the temperature falls down. If the temperature falls below the combination -reaction- point, then the reaction comes to a standstill. Therefore to such reactions external heat is essential.

Burning of the ordinary substances continues, because the temperature is steadily kept up by the heat liberated from the combinations -as these are exothermic- but like oxygen and nitrogen if heat is absorbed then they do not combine.

The rest of the very many conditions mentioned, catalytic agents, pressure, electricity, friction, etc. can easily be classed under one or the other of the chief three factors.

CHAPTER IV.

Types of Reactions.

After having considered the conditions that are essential for a chemical reaction to take place, the next step naturally is the consideration of the various possibilities *i. e.* types of reactions. We have already seen that when reaction is taking place there is bound to be some change in the heat quantity of the reacting substances and in the products of the reaction. According to this increase or decrease of heat quantity, the reactions have been classified as 'Exothermic' or 'Endothermic'.

Apart from the consideration of heat, there are points according to which the reactions may be classified, and these are with reference to the behaviour of the substances with regard to themselves. These are: (1) Combination or Direct union, (2) Decomposition, (3) Substitution, or Single decomposition, (4) Double decomposition, (5) Dissociation, (6) Allotropy (7) Polymerism, and (8) Isomerism.

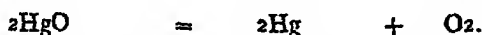
- i. **Combination or Direct union:** Reaction by which two bodies A and B, elementary or compound, unite (by addition of their masses) so as to form a new body -compound- AB is called combination.

	A	+	B	=	AB
	(before the reaction)				(after the reaction)
	mixture.				compound.
i	Hydrogen	+	Oxygen	=	Water.
	$2H_2$	+	O_2	=	$2H_2O$.
ii	Barium oxide	+	Oxygen	=	Barium dioxide.
	$2BaO$	+	O_2	=	$2BaO_2$
iii	Burnt lime	+	Carbon dioxide	=	Lime stone.
	CaO	+	CO_2	=	$CaCO_3$.

2. **Decomposition:** This is an inverse reaction by which a compound body splits up into its constituents which may be elements or compounds.



- i Oxide of mercury = Mercury + Oxygen.



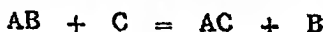
- ii Chlorate of potash = Chloride of potash + Oxygen.



- iii Lime stone = Burnt lime + Carbon dioxide.



3. **Substitution:** This is a reaction by which a body takes the place of another in a compound.



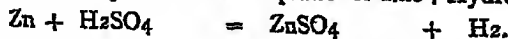
It is a case of decomposition of the primitive compound followed by combination.



- i Zinc + Hydrochloric acid = Chloride of zinc + Hydrogen.

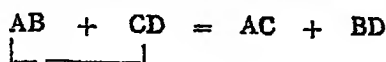


- ii Zinc + Sulphuric acid = Sulphate of zinc + Hydrogen.



4. **Double decomposition:** This is a case as the preceding one, but here both the components exchange their constituents and give rise to quite new products instead; *i.e.* it is a reaction by which two bodies AB and CD consisting of two elements, or of two atomic groups behaving like single atoms—radicals—(capable of entering in a

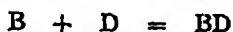
reaction) exchange their components, leading to the formation of two new bodies AC and BD.



It consists of two decompositions



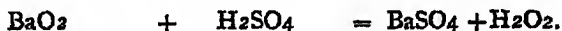
followed by two combinations.



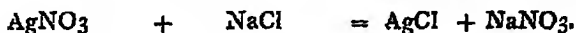
Double decomposition is the most common of the reactions. Combination is strictly speaking a double molecular decomposition.



- i Barium peroxide + Sulphuric acid = Hydrogen peroxide
+ Sulphate of barium.



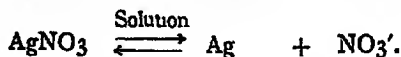
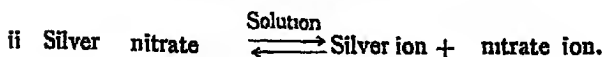
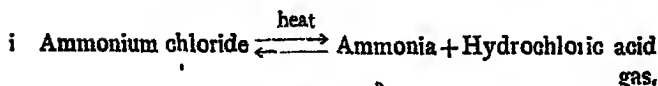
- ii Silver nitrate + Sodium chloride = Silver chloride
+ Sodium nitrate.



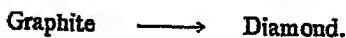
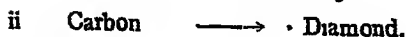
- 5 Dissociation: It is a reaction by which a body splits up into components capable of reuniting in the present conditions. It is therefore limited to the inverse reaction (réversible or balanced reaction). When a chemical compound splits up into simpler substances by change of physical conditions—temperature, pressure or dilution—and the products of the decomposition are capable of recombining to form the original compound, on

resumption of the original conditions, then the process of such decomposition is called dissociation.

It is of two kinds (1) Thermal and (2) Electrolytic.



6 Allotropy. It is a reaction characterized by a very important and *permanent* modification of the properties of a *simple* body, the substance being unaltered. This stands on the limit common to physical and chemical phenomena.

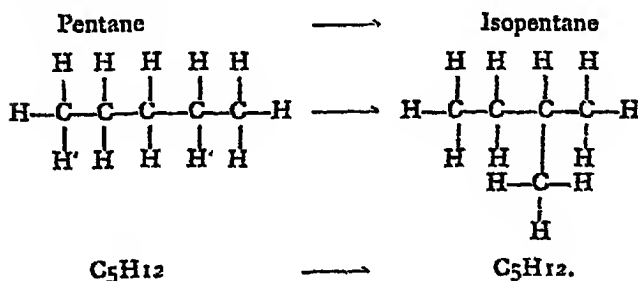


7. Polymerisation: This is very similar to the above allotropy with this difference that this refers to non-simple, i. e. compound—bodies, while allotropy is with reference to simple or elementary bodies.



- 8 **Isomerism.** This is a kind of reaction also characterized by a very important and permanent modification of a compound body whose centesimal composition remains unaltered. This is different from the latter -polymerisation- in this that, in polymerism the weight of the body -molecule- changes; while here it is constant.

Isomerism is a phenomenon of molecular condensation and decomposition



CHAPTER. V.

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The Laws of Chemical Combination.

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Having considered the composition of substances and their nature we may now go a step further. What generalizations have been reached with regard to the characteristics of a chemical reaction? What theoretical ideas have been developed as to the mechanism of these actions? These are the questions which naturally as a matter of consequence suggest themselves to us. Let us consider these now.

We have already seen (chapter III) that there are some special conditions necessary for a chemical reaction, and these chemical reactions are of different types. Not only this but in addition we have also noticed that reactions are either 'exothermic' or 'endothermic'. All these are chiefly with regard to the qualitative side of them but when chemical changes (reactions) were carefully examined from a quantitative point of view, four laws were discovered in obedience to which chemical actions take place. These laws are styled as 'The laws of chemical combination' and are :—(1) The Laws of Conservation of Mass (2) The Law of Constant Proportions, (3) The Law of Multiple Proportions (4) The Law Reciprocal Proportions.

I The law of conservation of mass or of weights.

"The Weight of a compound is equal to the sum of the weights of the different elements forming that compound" (*Lavoisier*).

In the earlier stages of the development of chemistry little or no importance was attached to the relations by weight between different reacting substances, and thus in the beginning it was believed that the total weight remained

constant and the difference in the result was due to the escape of 'heat,' 'light' and 'phlogiston,' all of which were considered as materials.

Phlogiston theory of combustion.

'Of all the conceptions which have been held at different times, that which is known as 'The Phlogiston Theory' had by far the greatest influence upon the development of chemistry. This theory was advanced by Becher (1635—1682) and was greatly extended and developed by the distinguished German professor Stahl (1660—1734). According to this theory every combustible substance contains more or less of a material or 'principle,' called phlogiston, [phlego = to burn] the escape of which constitutes combustion. The ash remaining, presents the original substance minus phlogiston. Substances which leave no ash are almost pure phlogiston.

When it is remembered that, at that time gases were little understood, oxygen unknown, and heat and light regarded as material substances given off during combustion, and that in this process something evidently did escape (namely the gaseous oxides), it will be seen that the theory was a reasonable one. It was known that materials increased in weight during combustion, but little importance was attached at that time to weight relations, and some adherents of that theory even assumed that phlogiston had negative weight *i.e.* weighed less than nothing. It was also difficult to explain why combustion required the presence of air. This theory was almost universally held for a hundred years, and was given up only after oxygen had been discovered and Lavoisier had demonstrated the true nature of combustion."

The "Law of Conservation of Mass" states that the total (weight) mass of the substance taking part in a chemical change remains constant (before and after the change). This law is the outcome of the experimental fact that in spite of the most painstaking care every time *all* the substances taking part in a chemical reaction are weighed before and after the change, there is no sign of any alteration in the quantity of matter.

This law is sometimes called the law of **Indestructibility of Matter**. If A and B represent separately the weights of two substances which take part in a chemical reaction, and produce the weights M and N of two other substances then according to this law of conservation of mass :



The question as to whether there is any change in the weights in a chemical reaction, has been investigated by Landolt and Heysweiller.

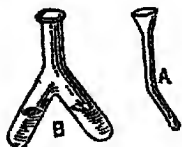


Fig 1.

A silver nitrate solution is introduced into one limb of Y shaped tube B Fig. 1. by means of a funnel A, and the solution of potassium dichromate into the other limb

The limb is then weighed and tilted so as to mix the solutions and start the reaction. No difference in the weight of the tube is noticed, before and after the reaction. After an examination of fifteen different reactions Landolt failed to detect any variation in the weight and this proves the validity of the law of conservation of mass.

II. The Law of Constant Proportion or Definite Composition.

‘ The same compound always contains the same elements combined together in the same proportion by weight ’ (*Proust*)

or

“ The weights of the constituent elements of every compound bear an unalterable ratio to each other, and to the weight of the compound formed.”

or

The same body has always the same composition

Stas prepared silver chloride from metallic silver in a variety of ways and at different temperatures and obtained the following results :—

Weight of silver.		Weight of silver chloride.	
1.	91.46 grms.	121.49	grms.
2.	69.86 "	92.81	"
3.	101.51 "	134.86	"
4.	108.54 "	144.20	"
5.	399.65 "	530.92	"
6.	99.99 "	132.82	"
7.	98.31 "	130.60	"

From the above numbers if we calculate the weight of chlorine over a fixed weight of silver in the silver chloride we get the following results :—

I.	1	Silver	:	0.3284	chlorine.
II.	1	"	:	0.3284	"
III.	1	"	:	0.3284	"
IV.	1	"	:	0.3284	"
V.	1	"	.	0.3285	"
VI.	1	"	.	0.3284	"
VII.	1	"	.	0.3284	"

From the above results it follows that the compound silver chloride is formed by the combination of silver and chlorine in the same proportions within the limits of experimental error. This holds good not only for silver chloride but for all compounds and still further it is evident that whatever be the source of the reacting elements or compounds the substances formed by the union of the same elements (or compounds) have also the same ratio of combination. This experimental fact is called the "Law of Constant Proportion."

Examples :

(1) In an experiment 1.317 grms. of tin were treated with nitric acid, and the resulting product ignited to constant weight. The weight of the resulting stannic oxide was found to be 1.672 grms.

In a second experiment 1.794 grms. of stannic oxide were reduced to metallic condition by heating with charcoal and the weight of the metal obtained was 1.414 grms.

Show that the results of these experiments are in agreement with the Law of Constant Proportions.

(2) The composition of silver chloride (AgCl) was determined in two ways as follows :—

(i) 0.956 gm. of silver is dissolved in nitric acid, and then precipitated as chloride by the addition of hydrochloric acid (HCl). The weight of silver chloride formed was 1.269 grms.

(ii) 1.758 grms. of silver chloride was reduced to the metal by heating in a current of hydrogen. The weight of silver formed was 1.324 grms.

Show that these numbers are in agreement with the Law of Definite Proportions.

III. The Law of Multiple Proportions.

"When the same two elements combine together to form more than one compound, the definite weights of one of the elements which combine with a constant weight of the other bear a simple ratio to one another" (*Dalton*)

or

"When one element unites with another in two or more different proportions by weight these proportions are simple multiples of a common factor."

Proust studied the composition of several pairs of compounds formed of the same two elements and put them in tabular forms as :—

Hydrogen.	Oxygen.	Copper.	Oxygen.	Tin.	Oxygen.
I. 11 %	89 %	80 %	20 %	78.4 %	21.6 %
II. 6 %	94 %	88.7 %	11.3 %	87.0 %	13.0 %

Proust could gather nothing from these simple percentage compositions, but later on Dalton and others found out a striking relationship in these cases and showed that if the composition is stated not in percentages but in weights of one element combined with a fixed weight of another then these weights fall, in the ratio of integer numbers :-viz :-

If the above percentage ratios are recast with reference to a fixed weight of one of the combining weights then we have —

Hydrogen.		Oxygen.	Copper.		Oxygen.	Tin		Oxygen.	
I.	2	:	1	:	1	:	1	:	2
II.	1	.	1	:	2	.	1	.	1

Similar facts led Dalton to enunciate the law of Multiple Proportions. When two elements A and B form more than one compound the weights of the element A, which combine with a fixed weight of the element B, stand in the ratio of small integers to each other. The most usual ratios are 1 . 1
1 : 2, 1 : 3, 2 : 3, and 2 : 5.

Examples.

(1) In three experiments the following weights of Litharge (PbO), Lead dioxide (PbO_2) and Red lead (Pb_3O_4) were respectively reduced in a current of hydrogen; 2.173 grms 1.949 grms. and 2.316 grms. The weights of lead remaining were respectively 2.017 grms. 1.688 grms and 2.10 grms

Show that these results illustrate the Law of Multiple Proportions.

(2) 2.461 grms of crystallized zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were dried at 100°C . The loss in weight amounted to 0.926 grms. The temperature was then raised to dull redness, when there was a further loss in weight of 0.154 grms and the anhydrous salt remained. Show that these results are in accordance with the law of Multiple Proportions.

IV. The Law of Reciprocal Proportions or
The Law of Equivalent Proportions or
The Law of Combining Weights.

"The weights of different elements which combine separately with one and the same weight of another element, are either the same as, or are simple multiples of, the weights of these different elements which combine with each other."

or

"The proportions in which two bodies A and B combine with a third C is also the proportion in which they unite with all other bodies as well as with one another" (*Richter and Wenzel*)

or

"The relative proportions by weight in which the elements A, B, C, D, combine with a constant weight of another element X, are the same for their combinations with any other element Z"

A German chemist by name Richter was of a mathematical turn of mind, and was interested in studying the numerical relations between the weights of different combining substances. His studies were chiefly with substances that are known as acids and bases. But the very same relations exist with regard to elements too.

If we take a number of elements, say A, B, C, D, E etc. which have chemical affinity between themselves, and then select, say a certain weight of A, of these as the one with which each of B, C, D, etc. is made to combine, then it will be found that :—

- (1) The different weights of B, C, D, E, etc. are to be substituted for each other for the same weight of A.
- (2) The different weights that combine with a fixed weight of A, are equal in chemical strength (affinity).

- (3) If B, C, D, E, etc. want to combine amongst themselves then also the above weights of each will be the weights that are necessary for the formation of the different compounds.
- (4) Thus these weights are (1) equal in value (2) can substitute one another, and (3) are such as also will be the weights for mutual combination and hence they are called (1) Equivalent weights, (2) Reciprocal weights or (3) Combining weights.

To be more concrete let us take the results obtained by the chemical analysis of a number of oxygen compounds :—

Water	...	hydrogen	11.18 %	oxygen	88.81 %
Chlorine monoxide		chlorine	81.58 %	"	18.41 %
Mercuric oxide	...	Mercury	92.59 %	"	7.41 %
Copper oxide	...	copper	79.90 %	"	20.10 %
Silver oxide	...	silver	93.09 %	"	6.90 %

The above results are so calculated that the sum of the constituents is 100, within the limits of experimental error. Taking oxygen as the standard, let us calculate what amount of each of the other elements will combine with a given quantity say 1 gram of the selected element. Collecting together the results of the calculations we get the following numbers which are combining with oxygen.

Oxygen.	Hydrogen.	Chlorine.	Mercury.	Copper.	Silver.
1.	0.126	4.431	12.5	3.975	13.496

Now all of these elements hydrogen, mercury, copper and silver combine with chlorine forming chlorides. The chlorides of these elements are found on analysis to have the following percentage composition :—

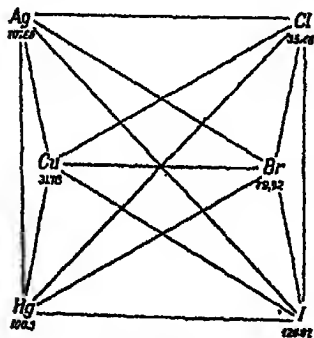
		per cent.		per cent.
Hydrogen chloride	Hydrogen	2.76	Chlorine	97.23
Mercuric	Mercury	73.80	"	26.20
Cupric	Copper	47.30	"	52.70
Silver	Silver	75.26	"	24.74

From the analysis of the chlorides, let us calculate the amount of the elements which will combine not with 1 gram but with 4.431 grams of chlorine. Collecting together the results of the calculations we get :—

Chlorine. Hydrogen. Mercury. Copper. Silver.

4.431 0.126 12.5 3.975 13.496

On examining the two sets of results that we have obtained, we find that 4.431 grams of chlorine and 0.126 gram of hydrogen, which combine with 1 gram of oxygen, also combine with one another to form hydrogen chloride.



This similarity of results we find also in the case of mercuric chloride, cupric chloride and silver chloride.

Fig. 2

Fig -2

This law of equivalent or reciprocal proportions is better illustrated by the following graphic scheme:—

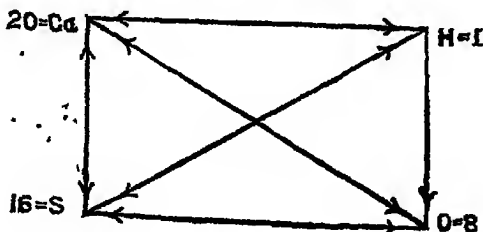


Fig.-3.

The four corners of the rectangle fig. 3. are occupied by the four elements, Hydrogen, Calcium, Sulphur and Oxygen. The numerals present the quantities that will combine with 1 gram of hydrogen, and the arrows represent the different possible combinations.

This shows that 20 grams of calcium and 8 grams of oxygen which combine with 1 gram of hydrogen also combine together to form calcium oxide (CaO). Other similar combinations can be seen to be substantiated by following Fig. 4.

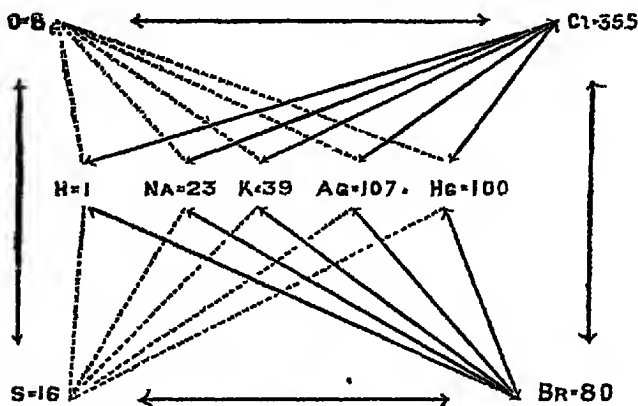


Fig.-4

This law is important and is so in this respect that, it facilitates our work of determining the proportions in which elements will combine to form compounds. It is only necessary to find once for all the combining weights *i. e.* the weights of the various elements which will combine with a fixed weight of any one element selected as the standard.

The choice of the Standard is arbitrary and making the selection we only look to our convenience. Dalton selected hydrogen as the standard, for it is the lightest of all the known elements, and adopted 1 as the equivalent weight for hydrogen. On the other hand Berzelius selected oxygen as the standard and fixed 8 as the combining weight for oxygen, for formerly

it was believed that in water 8 parts by weight of oxygen are in combination with 1 part by weight of hydrogen. Of the two standards oxygen has the advantage over hydrogen in this that almost all the elements combine with it, to form well defined compounds, so that the combining weights of other elements can be directly determined by the analysis of their oxygen compounds. However the use of either of these two elements made no difference as long as the ratio of the combining weights of hydrogen and of oxygen was considered to be 1 : 8. Recently Morley and others by the accurate analysis of water showed that the ratio is not 1 : 8 but is 1 : 7.94. In other words if the combining weight of hydrogen be 1, the combining weight for oxygen will be 7.94 and not 8. Since the combining weights of the majority of elements are determined by the analysis of their oxygen compounds on the assumption that the combining weight of oxygen is 8, every time a more accurate analysis of water is made, the combining weights must necessarily be recalculated, if hydrogen be retained as one of the standards. To avoid this difficulty hydrogen is not selected as the standard but oxygen is selected with 8 as its combining weight and the combining weight of hydrogen is calculated from the results of the analysis of water, which according to

Morley is $\frac{8}{7.94} = 1.008$.

Besides this reason there is another advantage in selecting O = 8 as the standard. If the combining weight of oxygen is taken as 8 then its atomic weight becomes 16. When the atomic weight of oxygen is taken as 16, it is found that a large number of elements have atomic weights more closely approximating to round numbers than in the case when the weight of hydrogen is taken as unity, so that the chemical calculations are simplified. Thus with hydrogen = 1.00 we have :—

Boron. Carbon. Columbium. Gallium. Manganese. Mercury

10.9	11.91	93.3	69.5	54.6	198.5
------	-------	------	------	------	-------

whereas taking oxygen standard these figures become:

Boron. Carbon. Columbium. Gallium. Manganese. Mercury.

11	12	94	70	55	200
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Thus in chemical arithmetic we in this way get rid of fractions, which simplifies calculations.

Thus now fixing one standard "Oxygen = 8", if calculations are made from the analysis of the oxides of the various elements that will combine with 8 grms. of oxygen—the standard—we get the following results.—

Oxygen. Hydrogen. Chlorine. Mercury. Copper. Silver. etc.

8	1.008	35.45	100	31.8	107.88
---	-------	-------	-----	------	--------

These numbers are the different weights of various elements that combine with 8 grams of oxygen our standard, hence these are called the 'Combining weights'

According to the law of reciprocal proportions "whenever elements combine to form compounds they will always combine in the ratio of their combining weights." This deduction which is the direct outcome of the law of Reciprocal Proportions is known as the law of Combining Weights.

The combining weights also represent the ratios in which elements displace each other (above graphic representations pages 41, 42,) in the compounds Water H_2O for example contains 6 parts by weight of oxygen to 1 part by weight of hydrogen. But when oxygen is replaced by sulphur forming hydrogen sulphide H_2S , the new compound is found to contain 16 parts by weight of sulphur. Thus 16 parts by weight of sulphur are equivalent to eight parts by weight of oxygen. For this reason the combining weights are often termed, equivalent weights Thus :—

The combining weight or the equivalent weight of an element is that quantity of it which combines with or displaces 8 parts by weight of oxygen or the quantity of any other element equivalent to 8 parts by weight of oxygen

Different equivalents for the same elements.

The equivalent weight of an element depends upon the particular compound employed in the determination. Thus if

for example we determine the equivalent weight of carbon from the composition of the monoxide (CO) we obtain the value as 6. But instead if the dioxide (CO₂) were employed, the value for carbon would be 3.

Equivalent weights of compounds

The term equivalent weight can be extended to compounds. The equivalent weight of a compound refers only to the particular reaction of the compound under consideration. If we are considering the neutralization of acids and bases, we may define the equivalent weight of an acid as that weight of it which contains one part by weight of the replaceable hydrogen. The equivalent of a base is then that weight which can be neutralized by an equivalent weight of an acid. In the case of an oxidising agent the equivalent weight is that weight of it which can perform function, equivalent to the oxidation of one part by weight of hydrogen.

The methods employed in the determination of equivalent weights are :—

- (1) The replacement of hydrogen in acids by metals.
- (2) The replacement of a metal in a salt by another metal.
- (3) The oxidation of an element.
- (4) The reduction of oxides by hydrogen
- (5) The decomposition of salts by heat.
- (6) The neutralization of acids by alkalis or by carbonates.
- (7) The electrolytic method based on Faraday's law.
- (8) The determination of gaseous densities and ratios of combination by volume of gases.

Examples ;—

- (1) 0.321 gram. of magnesium when heated in air yielded 0.531 grm. of the oxide of the metal. Find the equivalent weight of the metal. (12.23.)

CHAPTER VI.

Chemical Notation.

All the chemical actions and reactions that are taking place need to be expressed when these reactions are being discussed or described. If we adopt the system of full explanations in detail without adopting convenient abbreviations then the explanations not only become lengthy and often times too verbose, nay they even become so complicated as not to be grasped quickly and clearly. To avoid the above inconvenience and to facilitate both expression and explanation, abbreviations and mathematical methods are introduced also into chemical language. Thus in short chemistry has its own language.


































Symbol The names of the different elements are represented by 'symbols' [symbollo=to infer] which consist of the initial letters of their Latin names, followed at times by a smaller letter to avoid confusion.

Formerly the writing of the symbols was of a different kind. The symbols were adopted, not with reference to the name of the element, but with reference to the quality of the element and this led to confusion due to the same symbol standing at times for two or more elements. Thus Dalton imagined *the atoms to be small spheres* and represented the atoms of the different elements by various symbols enclosed in a ring or a circle



Atoms of metallic elements were represented by circles containing the initial letters of their names.

OLD CHEMICAL SYMBOLS & FORMULÆ.

 air	 iron	 platinum	 acid
 fire	 gold	 silver	 nitre
 water	 lead	 sulphur	 acetic acid
 antimony	 mercury	 tin	 crystal
 arsenic	 corrosive sublimate	 zinc	 precipitate
 bismuth	 mercury precipitate	 caustic lime	 purified
 copper	 nickel	 sal ammo-mac	 sublimed
 Oil  cinnabar  realgar  salt  caustic alkali			

Berzelius *omitted* the circles and retained the initials. To avoid further complications this a well formed system was adopted by which the initial letters are selected. This is now the universally adopted system of notation.

As said already if the initial letters are the same, then the initial letter together with the next following is selected for the symbol; thus: Hydrogen and Helium are represented by 'H' and 'He' respectively. But sometime even this make-shift fails to avoid confusion because even the second letters are also identical.

Thus:

Chlorine has C and h.

Chromium has C and h.

or

Carbon has C and a.

Calcium has C and a.

Cæsium has C and a.

Cadmium has C and a.

When such conditions prevail the second common letter is dropped and the third letter in order is selected for symbol purposes. Thus:

Calcium has Ca as the symbol.

Cæsium has Cs „ „ „

Cadmium has Cd „ „ „

Symbol weight. A symbol does not merely stand for the name of the element but it stands also for:

- (1) one atom of the element and
- (2) a definite weight of it, namely a weight proportional to its atomic weight.

Thus H or O stands not only for one atom of hydrogen or that of oxygen but also stands for 1 gram the weight of an atom of hydrogen or 16 grams the weight of an atom of oxygen. Such weights expressed in grams are called the symbol weights of the elements.

Formulas. Compounds being bodies of complex nature *i. e.*, made up of more than one kind of atoms are represented by a '*complex symbol*' called "*molecular formula*" or simply "*formula*." It is obtained by placing in juxtaposition the symbols of the atoms which make up the molecule. It represents an aggregate of atoms.

Now when the composition of a compound is to be represented in terms of the mutual quantities that take part in forming the compound, then the first and the foremost thing that suggests to us is that we might disregard the symbol weight and the symbol used thus. Fe, 63.52 per cent, S, 36.48 per cent, (instead of the weights 56 = Fe and 32 = S). But this is awkward. Instead of representing the composition in percentage composition, it is better to express it by stating the number of symbol-weights of each element present in a

combining weight of the compound. Thus the symbols FeS represent a compound made up of one symbol weight of iron and one of sulphur, namely 55.84 parts of iron to 32.07 parts of sulphur making a total of 87.91 parts of iron sulphide.

To convert such weights into percentages, knowing that the latter are parts per hundred, we need only solve the proportions :

$$87.91 : 55.84 \quad . \quad 100 : X = 63.53 \text{ percent iron.}$$

$$87.91 : 32.07 \quad :: \quad 100 : X = 36.48 \text{ percent sulphur.}$$

Symbols used in this way constitute the formula of a compound.

To derive a formula from the percentage composition.

Chemical analysis gives us the different percentages of the elements that are forming the compound, but this does not tell us in any way as to the number of atoms of each element that are in the molecule under examination *i. e.* it does not give us the integer number of atoms forming the compounds but only gives the total quantities of weights. This we know is not what actually is when combinations are taking place. We know that combinations take place with regard to full *i. e.* integer number of atoms and not fractions of atoms. Thus if we want to give expression to what is the actual method of combination we must arrive at the number of the different atoms in the molecule.

Upon the percentage basis the molecular weight is regarded as brought over to the value 100. This number, however, gives in itself no clue to the probable molecular weight of the compound nor the number of the different atoms present in the molecule. The percentage amounts of the proportional parts of the total molecular weight always agree with the exact quantity of each element present in one molecular weight of the compound. Having adopted 100 as the molecular weight, each percentage amount becomes the accepted value for the formula-quantity of that particular

element in the molecular weight (formula). If now we divide each of these percentage values by the atomic weight of the corresponding element, we obtain not whole numbers, indicating the number of atomic weights of the respective elements present, but fractions or better factors of these whole numbers, all of which are related to the true numbers in the same ratio as the adopted value *i. e.* 100 is to the real molecular weight.

Since we know that compounds are formed of whole number of atoms, a chemical formula necessarily calls for simple multiples of the atomic weights of the concerned elements. To get this we have only to raise the entire range of factors by some term which will bring each and every one of it into whole numbers. Thus when the smallest factor is made the divisor, then all the other factors, divided through by it must give quotients which are equal to or greater than the smallest factor taken as *unity*.

This will give the number of atoms of each elements. In short the method for converting percentage weights into formula is .

Percentage weights to be converted into the formula.
Weights.

- (1) Take the different percentage weights and divide them by their individual atomic weights.
- (2) Divide the numbers *i. e.* quotients, got from (1), by the smallest of them.
- (3) The quotients that are got give the number of atoms of each element.

Examples :

Find the formula for potassium chlorate when the result of analysis is the following :—

$K=31.91\%$; $Cl=38.93\%$; and $O=39.19\%$.

- (i) Atomic weights are $K=39.10$; $Cl=35.5$ & $O=16.00$.

∴ by dividing the percentage by the atomic weights we get.

$$0.8161 : 0.159 : 2.447$$

(ii) Each divided by 0.159 the smallest number we get

$$1 : 1 : 3$$

∴ The formula is KClO_3 .

(2) Derive the formulæ of the following substances the composition of which is found to be :—

(i) $\text{N} = 30.43$ $\text{O} = 69.57$ <hr style="width: 100%;"/> 100.00	(ii) $\text{Fe} = 70.01$ $\text{O} = 29.99$ <hr style="width: 100%;"/> 100.00	(iii) $\text{Ca} = 38.72$ $\text{P} = 20.00$ $\text{O} = 41.28$ <hr style="width: 100%;"/> 100.00
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(iv) $\text{K} = 45.95$ $\text{N} = 16.45$ $\text{O} = 37.60$ <hr style="width: 100%;"/> 100.00	(v) $\text{K} = 28.73$ $\text{H} = 0.73$ $\text{S} = 23.52$ $\text{O} = 47.02$ <hr style="width: 100%;"/> 100.00	(vi) $\text{Mg} = 9.16$ $\text{S} = 16.01$ $\text{O} = 26.01$ $\text{water} = 51.22$ <hr style="width: 100%;"/> 100.00
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[(i) NO_2 ; (ii) Fe_2O_3 ; (iii) $\text{Ca}_3(\text{PO}_4)_2$; (iv) KNO_2 ; (v) KHSO_4 ; (vi) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.]

(3) Derive the formula of the substance which on analysis gave the following composition :—

$$\begin{aligned} \text{C} &= 85.45\% \\ \text{H} &= 14.64\% \end{aligned} \quad \dots (\text{CH}_2)$$

(4) Derive the formula of that compound of hydrogen and oxygen which gave by analysis 5.93 % hydrogen. A determination of its molecular weight gave the value 33.8.

$$\dots (\text{H}_2\text{O}_2)$$

(5) Derive the formula of that oxide of nitrogen which gave by analysis 30.4 % nitrogen. In the solid state it was

found to have a molecular weight of 92.4, whereas, the actual density of its vapour above 140°C was only 20.13.

... (Solid N_2O_4 ; gas NO_2 .)

6) Derive the formula of crystallized copper sulphate, 7.84 grams of which lost 2.79 grams of water upon dehydration.

... ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)

7) Derive the formula of the crystallized salt which by analysis gave the following percentage composition. —

$$\text{Fe} = 19.98 \%$$

$$\text{S} = 11.47 \%$$

$$\text{H} = 5.24 \%$$

$$\text{O} = 63.31 \%$$

$$100.00$$

10 grams of this crystallized salt lost 4.5 grams of water upon dehydration.

... ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

Calculation of the percentage composition of a given compound.

The percentage composition can be determined by either synthetical or preferably chemical means. Thus it is found that:

10 grams of magnesium combine with 6.88 grams of oxygen to form magnesium oxide MgO .

This ratio will be found to hold for all quantities of Mg or MgO .

Hence 100 grams are taken as the basis, the $\frac{10}{16.88}$ of 100 i. e. 60.3 will be the amount of Mg in 100 grams of MgO .

Similarly for oxygen :—

$$\frac{6.55}{16.88} \text{ of } 100 = 39.7 \%$$

hence

$$\begin{array}{rclcl}
 \text{MgO} & . & \text{Mg} & :: & 100 & : & X \\
 16.58 & \cdot & 10 & : & 100 & : & X \\
 & & & & & & = 60.3 \%
 \end{array}$$

Hence the percentage composition is

$$\text{Mg} = 60.3 \% ; \text{O} = 39.7 \%$$

Examples :

(1) What weight of sodium (Na) is present in 50 grams of sodium nitrate (NaNO_3) ? ... (13.55 grms.)

(2) What weight of oxygen is present in 50 grams of sodium bicarbonate (NaHCO_3) ? ... (28.57 grms)

(3) What weight of mercuric oxide (HgO) will contain 30 grams of oxygen ? ... (405 grms.)

(4) What weight of sulphuric acid (H_2SO_4) can be prepared from 100 grams of sulphur ? ... (306.25 grms.)

(5) Calculate the percentage purity of a sample of horn silver (AgCl) which analysed for 74.2 per cent silver.
... (99.04 %)

(6) Calculate the percentage purity of a sample of marble (CaCO_3) which analysed for 39.6 per cent calcium. ... (99 %)

(7) Determine the percentage amount of water in crystallized sodium carbonate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (62.93 %)

(8) Calculate the percentage of potassium chloride in a sample of carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) which analysed for 37.72 per cent chlorine. ... (26.8 %)

(9) Determine the percentage composition of calcium carbonate. ($\text{Ca} = 40.05 \% ; \text{C} = 11.99 \% ; \text{O} = 47.96 \% .$)

(10) Determine the percentage composition of crystallized sodium sulphate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

$$(\text{Na} = 14.28 \% ; \text{S} = 9.95 \% ; \text{O} = 69.51 \% ; \text{H} = 6.26 \%)$$

N. B:—

I. Special rules for writing down the chemical formula.

- (i) The electro negative element is written last.
- (ii) If one of the components is to be found in the compound in a proportion which is 2, 3, 4.....times as great as the proportional number, the fact is indicated by writing the number 2, 3, 4..... in small characters on the right of the symbol and a little below e. g. S_2, S_2, O_3, O_2 . This number affects the symbol only and has the value of an algebraic co-efficient.
- (iii) If the component which is found in the compound in several proportions, is itself of a compound nature (atomic group) it is to be placed between brackets and then treated as an ordinary symbol :



- (iv) Some molecular compounds seem to be the result of the fixation of water by an already fully constituted body, then the two formulæ that of the body, and that of water are written and separated by a comma, or by a full point or by the + sign.



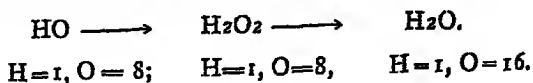
II. To convert a formula from the system of equivalents to the atomic system.

- (1) All elements have atomic weights equal to their equivalent weights, all the atomic weights are twice as great as the equivalent weights.

Then shall the two formulæ be the same.

- (2) Some of the elements have atomic weights equal to and some other elements have atomic weights twice as great as their equivalent weights.

Then double the symbols in the formula written in the system of equivalents and substitute weights. (There are however other considerations which are always to be taken into account).



Different Kinds of Formulæ.

After having considered the method of arriving at a chemical formula the next question naturally is: Is there only one kind of formula or are there different kinds of formulæ? The answer is in the affirmative. The different kinds of formulæ are—

- (1) Empirical
- (2) Molecular.
- (3) Constitutional.
- (4) Rational.
- (5) Graphic.

(1) **Empirical Formulæ.** These show the kind of elements contained in the molecule (determined by experiments: *e. analysis*) and the relative number of atoms of each element in the molecule.

They are experimentally determined and deduced from the percentage composition of the compound.

Examples:

(1) Carbon = 93.3 %; Hydrogen = 7.69 %

$$\therefore \text{C} = \frac{93.3}{12} = 7.69; \text{H} = \frac{7.69}{1} = 7.69.$$

\therefore the empirical formula is CH.

(2) Carbon 40.00 % Hydrogen 6.60 % Oxygen 53.40 %

$$\therefore \text{C} = 3.33; \text{H} = 6.6 \text{ and } \text{O} = 3.3.$$

\therefore CH₂O is the formula.

In the same way we would find CH_2 , FeCl_3 , HCO_2 , HgCl , CuClO_3 etc.

2) **Molecular Formulæ.** They show not only the kind and the relative number of atoms in the substance but also the true and absolute number of atoms in the molecule. They do not simply express the composition of the substance, but also the composition of a molecule of a substance.

(∞) In the case of the elements they are obtained by the experimental determination of vapour densities and atomic weights: H_2 , P_4 , Cl_2 , O_2 , O_3 , Hg , Cd and Zn .

(β) In the case of compounds they are calculated from the empirical formulæ and the molecular weights.

(a) The molecular weight of the substance CH in example (1) is found to be 26.

$\therefore \text{C}_2\text{H}_2$ is the molecular formula.

(b) If we suppose a substance whose empirical formula is CH_2O has $M \text{ Wt.} = 30$, then we find that it agrees with the molecular weight of Formaldehyde.

$\therefore \text{CH}_2\text{O}$ is the formula of formaldehyde.

(c) The molecular weight of glucose is found to be 180. Then

$$C = \frac{40 \times 180}{100} = 6, \quad H = 12; \quad O = 6.$$

$\therefore \text{C}_6\text{H}_{12}\text{O}_6$ is the formula.

In like manner C_2H_4 , Fe_2Cl_6 , $\text{H}_2\text{C}_2\text{O}_4$, Hg_2Cl_2 , and $\text{Cu}_2\text{Cl}_2\text{O}_6$ may be fixed.

(3) **Constitutional Formulæ.** They show the reactions which the substances undergo on treatment with reagents. Thus H.CHO , $\text{H.C}_2\text{H}_3\text{O}_2$, $(\text{COOH})_2$; $\text{Cu}(\text{ClO}_3)_2$...etc.

Similarly more in detail :

- (1) $\text{NO}_2\text{Cl} + \text{H.OH} = \text{HCl} + \text{NO}_2.\text{OH}$ (*i. e.* HNO_3).
- (2) $\text{SO}_2 \text{ Cl}_2 + 2\text{H.OH} = 2\text{HCl} + \text{SO}_2.(\text{OH})_2$ (*i. e.* H_2SO_4).
- (3) $\text{PO.Cl}_3 + 3\text{H.OH} = 3\text{HCl} + \text{PO}.\text{(OH)}_3$ (*i. e.* H_3PO_4).

(4) **Rational Formulæ** These are arrived at by comparing the behaviour of the substance under consideration with other substances of the same type Thus —

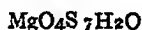
For sulphuric acid we write H_2SO_4 and not SH_2O_4 and for calcium carbonate also CaCO_3 and not CCaO_3 .

N. B A compound has but one empirical and one molecular formula but it may be represented by quite a number of rational formulæ.

(i) A compound is found to have an empirical formula $\text{MgH}_{14}\text{SO}_{11}$ —

(1) Heated above 200°C , 7 molecules of water are given off

∴ The formula should be,



(ii) When heated to 100°C only 6 molecules of water are given off as vapour

∴ The formula should be $\text{MgO}_4\text{S H}_2\text{O } 6\text{H}_2\text{O}$.

(iii) The chemical reactions show the presence of the radical SO_4 .

∴ The formula should be $\text{MgSO}_4 \text{ H}_2\text{O } 6\text{H}_2\text{O}$ and this is the rational formula.

But suppose if we want to express the fact that this compound is derived from sulphuric acid $\text{SO}_2.(\text{OH})_2$, then $\text{SO}_2.\text{O}_2 \text{ Mg H}_2\text{O } 6\text{H}_2\text{O}$ will be the formula

or

If we desire to show that a sulphate is the result of the action of SO_3 on the oxide of the metal ($\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$) then the formula is —

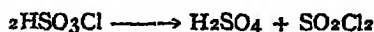


(8) Analysis shows that the formula for sulphuric acid ought to be SH_2O_4 . But

- (1) If we treat sulphuric acid with PCl_5 we get .—

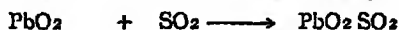
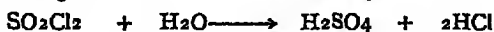
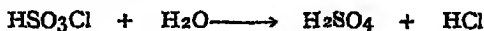


- (2) on heating the chlorosulphuric acid we get —



∴ $\text{SO}_2(\text{OH})_2$ is the formula,

and further confirmed by



But when zinc is acted upon by sulphuric acid then we get the following reaction —



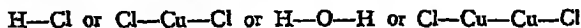
∴ H_2SO_4 is the formula

Sulphuric acid is obtained by the action of sulphur trioxide on water hence



(5) **Graphic Formulæ** They show the manner in which the valency of each atom in a molecule is supposed to be saturated

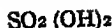
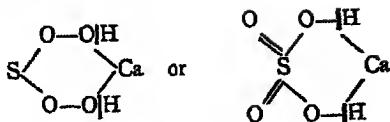
- (α) **Binary compounds** The valency of each element is to be ascertained, by attention being paid to the nature of the compound (ous or ic).



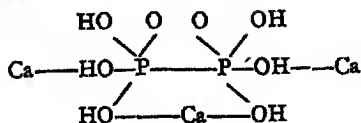
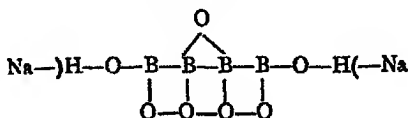
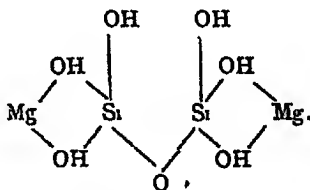
- (β) **Higher compounds.**

- (1) Write the formula of the acid
- (2) Put the hydroxyl radicals in evidence
- (3) Write the graphic formula of the hydroxides
- (4) Replace the hydrogen atoms by metals or radicals, bearing in mind the valency of the latter

Thus for calcium sulphate CaSO_4



or for calcium phosphate

or $\text{Na}_2\text{B}_4\text{O}_7$ or $\text{Mg}_2\text{Si}_2\text{H}_2\text{O}_7$.

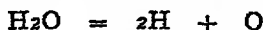
Chemical Equations. Formulæ express only the composition of substances but if these very substances interact then what is to be done to show the quantities that are taken and also to express the quantities and the different kinds of products that are formed? Not only can the composition be expressed by formulæ, but the changes taking place in chemical reactions can be very well represented in the form of equations. Because we know for certain from the 'law of conservation of mass' that the original and the final product must be equal in quantity, Thus :—

A chemical equation is an expression used to represent a chemical reaction. The bodies which enter into the reaction form the left-hand members of the equation, and the resultants of the reactions the right-hand members.

In every member of the equation the different formulæ are connected by the sign + and the two members are themselves connected by the sign = Thus :



In order that a chemical equation be correct and good, the number of atoms (or equivalents) of each element must be the same in the two members of the equation. Thus when water is decomposed by electricity we get —

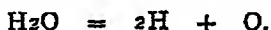


This equation is correct mathematically but chemically considered it is wrong because a chemical equation is not merely algebraic but indicates that all the products are really formed *i. e.* reactions must come out to be true For instance compare the equation —



Although this is a perfectly algebraically correct equation, still chemically it is quite wrong, since calcium oxide cannot be decomposed in this way.

The equation must be both qualitative and quantitative Not only this but the reaction quantities must be such that they must exist in the form represented. Thus :



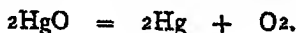
is correct both mathematically and qualitatively, but the hydrogen and oxygen as represented in the equation are impossible of free existence and hence cannot be coming out as gases in that form These must be in their molecular form. Sometimes the products of the reaction may be of such a nature as to require for the formation of one molecule the presence of several molecules of the reacting substances. The molecules of the bodies are then to be preceded by a number which behaves like an algebraic coefficient. Such coefficients might be calculated, but as a rule, a very simple reasoning will do to determine them.

We know that manganese dioxide MnO_2 is decomposed by heat so as to yield Mn_3O_4 and some free O. We should write 3MnO_2 as the left hand member, since the molecule of the new compound contains Mn_3 and this leads us to take 3O_2 or O_6 . But since the molecule of Mn_3O_4 keeps O_4 we conclude that O_2 is set free. Thus.



N. B.

The molecules of metals or solids under normal conditions are not yet determined and hence the metals have to be represented in the simplest form: *e.* atomic. Thus:



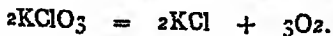
Chemical calculations.

The equations such as those ones which have been just explained are not merely a convenient form of recording the results of experiments, but they represent the composition of substances, entering into reactions with one another and also the proportions by weight which take part in the reactions. But still further they also tell us the weights and composition of the products formed. Thus these can be very conveniently employed in solving problems that involve chemical transformations.

Examples.

(1) What weight of oxygen can be obtained by heating 40 grams of potassium chlorate?

The way in which potassium chlorate breaks up is:—



The formula weight of potassium chlorate is .

$$39 \cdot 1 + 35 \cdot 46 + 16 \times 3 = 122 \cdot 56.$$

Thus from the equation we know that two molecules: *e.* 245.12 grams of the chlorate give us 96 grams of oxygen. Hence by rule of three we get:

$$245.12 : 96 : 40 \cdot X$$

$$X = 15.66 \text{ grams.}$$

(2) What would be the weights of potassium chloride and oxygen respectively produced by complete decomposition of 6 grms. of potassium chlorate ?

... (3.65 grams KCl & 2.35 grms. O)

(3) Calculate the weight of hydrogen sulphide which would be formed by dissolving 4 grams of antimony sulphide in concentrated hydrochloric acid

.. (1.215 grms.)

(4) A gas bag has a capacity of 45 litres. How much manganese dioxide containing 70 % MnO_2 is required to fill it with oxygen at $15^\circ C$ and 760 mm. barometric pressure ?

... (710 grms.)

(5) 132.74 kilograms of hydrogen are needed to inflate a balloon. What weights of zinc and sulphuric acid will be required to produce this quantity of the gas ?

(4333.96 kilos Zn ; 6504.26 kilos H_2SO_4)

(6) A specimen of marble weighing five (5) grams evolved 2.1 grams of carbon dioxide (corresponding to a theoretical volume of 1162.5 c. c. at $20^\circ C$ and 750 mm.) when acted upon by an acid. Estimate the degree of purity, assuming that all of the carbonate was present as calcium carbonate

.. (95.45 %)

(7) What volume of hydrogen measured at $18^\circ C$ and 746.4 mm. pressure will be liberated by the action of aluminium upon 20 grams of sulphuric acid containing 41.5 per cent H_2SO_4 ?

... (1986 c. c.)

(8) Determine the purity of a sample of anhydrous sodium carbonate, 3 grams of which gave, by treatment with sulphuric acid and final ignition, 3.99 grams of sodium sulphate

. (99.5 %)

CHAPTER. VII

Gases and the laws that are pertaining to them.

Everybody is quite acquainted with the fact that the three different 'states' in which we see different things are only depending upon the temperature in individual cases. Gaseous state is the property of all substances if the necessary conditions, especially as to temperature, are got. In some cases the temperature is too high and in others the substances decompose before the necessary temperature is reached.

General properties of gases.

(1) Gases respond much more easily to alterations of temperature than liquids and solids.

(2) Gases change their volume with the change of pressure.

(3) Gases allow heat to pass through them without being perceptibly warmed, they are sometimes said to be transparent to heat; the scientific term is 'Diathermanous' [therm = heat; dia = through.]

(Similarly all gases can be liquefied, hence the term permanent gases is no more existing).

Characteristic of the gaseous state.

All gases as said above show a very remarkable property of changing their volume rapidly, and this brings out the two properties of 'expansibility' and 'compressibility'.

(1) **Expansibility.** A gas is known to be a substance the different particles of which remain as much away from each other as possible, and on this account all gases try to

expand indefinitely and so to distribute uniformly in the container. Distribution occurs with great rapidity if a gas is let in vacuum.

If the gas is set free in a space that is already occupied by another gas, then the distribution takes place slowly. This phenomenon of distribution or mixing of one gas into another is called 'diffusion'. On account of diffusion the gases become evenly mixed. It is to be well borne in mind that diffusion is the function of the physical state and not of the intrinsic property of the substance and thus takes place quite independently of the relative weights of the gases. Likewise unlike liquids gases of unequal densities once mixed have no tendency to separate in different layers. Complete and permanent diffusion is the characteristic of all gases.

(2) Compressibility. Liquids and solids are very little affected by pressure, but gases change their volumes by pressure in a surprising manner e. g. the volume of air pumped in a motor or cycle tyre.

To understand the laws or relations of the gases we must have them under some accepted standard conditions of temperature and pressure, under which all the measurements may be carried out.

(α) The Standard Pressure. The pressure on the surface of the sea or the air column above it is taken as the standard, and when this is measured by the height of the mercury column that is required to counter balance it, it is found to be 760 mm. of the length of the mercury column, if the measurements are taken at sea level and at latitude 45° and when the temperature of mercury is 0°C .

(β) The Standard Temperature. All gases expand or contract by change in the temperature, and the change that is found in a gas irrespective of its quality is that it shrinks or expands by $\frac{1}{273}$ of its original volume per degree change of temperature. Judging from this we arrive at the fact that the

lowest temperature that would be necessary for a gas which is at unit volume at 0°C must be -273°C and no further, and this is styled as the 'Absolute Zero.' At absolute zero *i. e.* -273°C the volume of a gas must be zero. This means that before such a temperature is reached all gases will have become liquids in which state the law will not apply.

This -273°C is the starting point of all the calculations based on temperature, but the common starting temperature being the temperature of the freezing point of water *i. e.* 0°C this 0°C is styled as the 'Normal temperature' and -273°C is styled the absolute as compared to normal *i. e.* 0°C .

Whenever measurements of volumes are to be made then one must remember that the volume is affected in proportion to that of the difference from the absolute zero, and hence all computations must be reduced to this absolute temperature.

So the conditions agreed as standard—taken common by all—are pressure at the sea level and the temperature at the freezing point of water at sea-level, and these are called the standard or better Normal Temperature and Pressure, or abbreviated into N. T. P.

(1) The Law of Boyle. (Relation of volume to pressure). The gases are affected by pressure and change their volumes in a regular fashion. Boyle has found the regularity and put it in the form of a law and it is "The volume of a gas, at constant temperature is inversely proportional to the pressure to which it is subjected". It can be expressed in the mathematical form thus :

$$V : V_1 :: P_1 : P \text{ i. e. } V \times P = V_1 \times P_1$$

$$V_1 = \frac{V \times P}{P_1}$$

This is evident from the following :—

Pressure	1	2	3	4	6	atmospheres.
Volume	12	6	4	3	2	litres.
Product	12	12	12	12	12	

Thus in the above case we find the product 12 remains a constant quantity.

Examples :

(1) 1000 c. c. of hydrogen are measured under a barometric pressure of 740 mm. What will the volume become under the standard pressure of 760 mm. ?

$$\text{The formula is } V_1 = \frac{V \times P}{P_1}$$

$$\begin{aligned} \text{by substituting. } V_1 &= \frac{1000 \times 740}{760} \\ &= 973.6 \text{ c. c.} \end{aligned}$$

(2) A given quantity of nitrogen occupies a volume of 360 c. c. under a pressure of 740 mm. of mercury. What will the volume become under normal pressure, assuming that the temperature remains unchanged ? ... (35.05 c c)

(3) In one of his experiments on the determination of the density of hydrogen, E.W.Morley found that the weight of 42.2023 litres of hydrogen at 0°C and 739.53 mm. was 3.6890 grams. Find the weight of a litre of the gas at N.T.P. .. (0.0898 grms.)

11. The Law of Gay Lussac (Charles). (Relation of volume to temperature). just as pressure changes the volume, so also the change in the heat quantity of the gas brings about the change in the volume of the gas, and this relation is expressed as . Gases under constant pressure expand (or contract) $\frac{1}{273}$ part of their volume at 0°C for every increase (or decrease) in temperature of 1°C. i.e. the volume of a gas varies directly as the temperature, the pressure remaining constant Thus mathematically it becomes.

$$V : V_1 : t \quad t_1$$

$$\text{i.e. } V \times t_1 = V_1 \times t$$

$$V_1 = \frac{V \times t_1}{t}$$

Examples :

(1) 10 c.c. of a gas are measured at 15°C . What volume will the gas occupy at 150°C , ?

Substituting the formula $V_1 = \frac{V \times t_1}{t}$

$$V_1 = \frac{10 \times (273 + 150)}{(273 + 10)}$$

$$= 14.69 \text{ c. c.}$$

N. B. While substituting 't' it is to be well remembered that the temperature is to be calculated from the absolute zero i. e. -273°C

(2) What will be the volume at 25°C . of 252 c.c. of oxygen measured at 15°C . -(260.75 c.c.)

(3) A gas has its temperature raised from 15°C to 50°C . At the latter temperature it measures 15 litres. What was the initial volume ? ... (13.3746 litres),

(4) The volume of a given mass of sulphur dioxide measured at 16°C was found to be 49.8 c.c. What would the volume become if the temperature were increased to 30°C pressure remaining unchanged ? ... (52.2 c.c.)

(5) A vessel of 2,000 c.c. capacity held 5 grams of a vapour at standard conditions of temperature and pressure. What weight of this vapour at 10°C and 750 mm. pressure can be held in this vessel, the capacity considered constant ? ... (4.76 grms.)

N. B.

A change of physical conditions i. e. solid, liquid or gaseous, of different substances requires different temperatures and pressures. Different quantities and different substances do require different physical energy in the above cases, but in the case of the special physical state i. e. gaseous, it is a peculiar thing. No matter what is the quality of the gas (i. e. whether a simple gas or a compound gas or a gaseous mixture) and the quantity of the gas it behaves always in the identical fashion when temperature (height of temperature) is made to bear influence upon

it. For every degree change in the temperature the volume changes by $\frac{1}{273}$ rd. of its original volume, irrespective of its quantity and quality, provided the pressure is maintained the same throughout the change.

III. Relation of Temperature and Pressure. If the volume be kept constant the pressure will increase in proportion to the temperature (absolute).

Combined effect of Boyle's and Charle's Law.

If a gas is simultaneously affected by both temperature and pressure, naturally both the laws will bear the effect on the volume of the gas, and hence as both are working, the result in the end will be the combined effect, and if both are made to act alternately, one after the other, or conjointly, the end result will be the same; and hence the combined laws may be represented as:—

(i) Boyle's law $V \propto \frac{1}{P}$ or $P_1 V_1 = P_2 V_2$

(ii) Charles' law $V \propto t$ or $\frac{V_1}{t_1} = \frac{V_2}{t_2}$

If these are expressed in terms of variation then

(a) V varies as $\frac{1}{P}$ or P varies as $\frac{1}{V}$ and

(b) V varies as t or t varies as V .

\therefore (a) and (b) combined

$$V \propto \frac{1}{P} \dots P_1 \propto \frac{1}{P_2} \quad t \propto t_2$$

$$VP = V_1 P_1 \dots t : t_1$$

$$V \cdot P \cdot t = V_1 \cdot P_1 \cdot t_1$$

$$V_1 = \frac{V \cdot P \cdot t_1}{P_1 \cdot t}$$

or as the calculations are always resolved to N.T.P. the formula will be

$$V_1 = \frac{V \cdot P \cdot 273}{760 \times t} \text{ for N.T.P.}$$

Examples

(1) 500 c. c. of chlorine are measured at 27°C and 750 mm. pressure. The temperature is increased to 77°C and the pressure to 1,000 mm. Find the new volume.

A sum like this can be worked in two ways. Firstly by solving the changes for the temperature and pressure individually, and secondly by arriving at the final volume by working out the effect in a joint fashion.

(\propto) Separate formulæ:

$$\begin{aligned} \text{(i) } \underline{\text{Boyles law.}} \quad V & \propto V_1 \therefore P_1 : P \\ & \quad 1000 : 750 \therefore 500 : V_1 \\ & \therefore \frac{750 \times 500}{1000} = 375. \end{aligned}$$

$$\begin{aligned} \text{(ii) } \underline{\text{Charles law.}} \quad V & \propto V_1 \therefore t_1 : t \\ & \quad (273 + 27) : (273 + 77) \therefore 375 : V \\ & \quad \frac{350 \times 375}{300} = 437.5. \end{aligned}$$

(8) Combined formula:

$$\begin{aligned} V_1 &= \frac{V \cdot P \cdot t_1}{P_1 \cdot t} \\ \frac{500 \times 750 \times (273 + 77)}{1000 \times (273 + 27)} &= 437.5. \end{aligned}$$

(2) A balloon containing 1,200 c. metres of coal gas under a pressure of 770 mm. of mercury ascends until the barometer stands at 530 mm. What volume would the gas in the balloon now occupy supposing none to have escaped.

... (1743.4 c. metres,

Henry's Law.

Gases like solids are soluble in liquids and their solubility is greatly influenced by circumstances with regard to temperature, pressure and the solvents.

With regard to temperature remembering Charles's law we can see that the solubility ought to get less and less as the temperature goes up, because the gases will try to expand and thus naturally will require more volume to occupy.

But with regard to the pressure influence, this question was studied by Henry, and he puts down his results in the form of the following law.

- (1) The solubility of a gas is proportional to the pressure at constant temperature, i.e. the more the pressure more the quantity of the gas that is dissolved.

(N. B. the solubility of a gas is always expressed in terms of 100 volumes of the solvent i.e. water and the dissolved volume of the gas in 100 volumes of the solvent)

There are two more statements of the same law, but the stand-points taken in defining it are different, and this brings about statements which apparently looks paradoxical though if the wording is carefully considered and the words properly understood nothing unusual can be found in them. The two statements are as follows :

- (2) The volume of a gas dissolving in a certain quantity of a liquid is independent of the pressure
- (3) The ratio of the concentration of the dissolved and the undissolved portion of a gas bear a constant ratio to each other.

The second statement of the law is equivalent to the first statement, because if the pressure is doubled the quantity of

the gas absorbed is doubled, but since its volume according to Boyle's law is halved, the original and the final volume absorbed is the same.

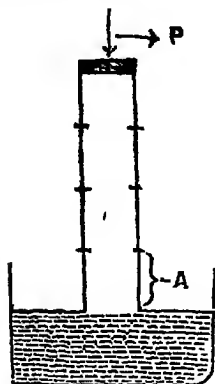


Fig 5

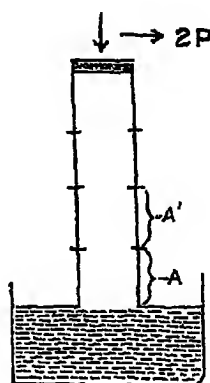


Fig 6

From figures 5 and 6 it can be seen that

$A \text{ vol.} + A' \text{ vol. at } p = A \text{ vol. at } 2p.$

$\therefore (A + A') \text{ vol} = A \text{ vol.}$

The same volume under p and $2p.$

The same volume.

This can be also proved mathematically thus :—

Suppose m grms. of the gas are contained in volume V at pressure $p.$

Then m grms. of the gas are contained in

volume $\frac{V}{2}$ at pressure $2p.$

If S is the solubility at pressure $p,$

then by Henry's law $2S$ is the solubility at pressure $2p.$

Now S grms. of the gas at pressure p are contained in a

volume equal to $\frac{SV}{m}$

and $2S$ grms. of the gas at pressure $2p$ are contained in a

$$\text{volume equal to } \frac{2S}{m} \times \frac{V}{2} = \frac{SV}{m},$$

i.e. the volumes of the gas dissolved at pressures p and $2p$ are identical and therefore independent of the pressure.

The third statement is also the same as the first, only the quantities and the volumes are disregarded but the number of particles or concentration of the dissolved and the undissolved volumes of the gas before and after the change of pressure are studied and their relations expressed in the form of a law.

Suppose the ratio in a given condition is $1 \cdot 50$. Then when the pressure is doubled the concentration both in space and in the water is doubled, but the ratio remains the same as the ratio is doubled both ways.

Again to put it in a mathematical form :—

Suppose m grms. of the gas are contained in volume V at pressure p ,

then m grms. of the gas are contained in volume $\frac{V}{2}$ at pressure $2p$.

If S is the solubility at pressure p ,

then $2S$ is the solubility at pressure $2p$,

and V is, say, the volume of the solvent. Then

At p .

$$\text{concentration of the dissolved gas} = \frac{S}{V}$$

$$\text{„ „ undissolved „} = \frac{m}{V}$$

$$\therefore \text{the ratio} = \frac{SV}{mV}.$$

At 2p

concentration of the dissolved gas = $\frac{2S}{V}$

„ „ undissolved „ = $\frac{2m}{V}$

the ratio = $\frac{SV}{mV}$

The ratios being equal it follows that the concentrations of the dissolved and the undissolved is the same.

N. B.

Henry's law is obeyed at moderate pressures and by gases which are not extremely soluble.

Ammonia (or sulphur dioxide or hydrogen chloride, etc.) does not obey Henry's law at ordinary temperatures when it is extremely soluble, but at 100°C when it is sparingly soluble it obeys this law.

As a corollary of the statement "A given volume of a liquid will absorb the same volume of a gas at all pressures" it follows that :

(a) A gas may be removed from a liquid if the solution is exposed in a space where vacuum is constantly kept.

(b) The same thing happens if a liquid charged with a gas is exposed in an atmosphere of another gas. The effect of the indifferent gas it is to retard the liberation of the first : the final effect is the same but a longer time is required e. g. aerated water.

(c) A gas may be made to replace another gas by sending a current of the first through the solution.

The following are the solubilities of gases.

100 vols. H ₂ O	dissolve at N.T.P.	105,000 vols. NH ₃ .	
"	"	50,500	" HCl.
"	"	8,000	" SO ₂ .
"	"	440	" H ₂ S.
"	"	180	" CO ₂ .
"	"	4	" O ₂ .
"	"	2	" N ₂ .

Examples.

(1) Given that at 4°C and a pressure of 760 mm of mercury 100 c.c. of water dissolve 0.00294 grms of nitrogen, calculate what weight of the gas would be dissolved in the same volume of water at the same temperature if the pressure were increased to 1600 mm of mercury

$$\begin{aligned}\text{weight of nitrogen dissolved at 760 mm. pressure} \\ = 0.00294 \text{ gm.}\end{aligned}$$

$$\text{By Henry's law } \frac{M}{V} = P.$$

$$\begin{aligned}\text{Weight of nitrogen dissolved at 1600 mm. pressure} \\ = 0.00294 \times \frac{1600}{760} \\ = 0.00619 \text{ gm.}\end{aligned}$$

(2) In an experiment it was found out that the weights of marsh gas and ethylene in 10 litres of water were respectively 0.321 gm. and 0.597 gm. Given that at the temperature of the experiment and at the normal pressure, 100 c.c. of water dissolve 0.00392 gm. of marsh gas and 0.0324 gm. of ethylene. Calculate the combined pressure of the two gases.

Here it naturally follows that the pressure due to the two different gases must be found first and then added up. The different steps for the same are as follows. —

(i) The volume of marsh gas dissolved in the given volume of water.

$$100 \times 0.00392 = 0.392 \text{ grms. of marsh gas.}$$

(ii) Next step is to calculate the pressure that would be required for dissolving the given weight 0.321 gm. of marsh gas.

$$\text{The pressure would be} = 760 \times \frac{0.321}{0.392} = 622 \text{ mm. mercury.}$$

(iii) The volume of ethylene dissolved in the given volume of water.

$$= 100 \times 0.0324 = 3.24 \text{ grms.}$$

(iv) The pressure required for dissolving the above weight 0.597 grm. of ethylene gas.

$$= 760 \times \frac{0.597}{3.24} = 140 \text{ mm. of mercury.}$$

The combined pressure therefore is .

Pressure of marsh gas = 622 mm. of mercury.

„ „ ethylene gas = 140 „ „ „

∴ combined pressure = 762 mm. of mercury.

(3) Given that the coefficient of absorption of carbon monoxide in water at 20°C is 0.01. Calculate the volume of the gas at 0°C which would be absorbed by 1.42 litres of water at 20°C.

The volume of a gas reduced to 0°C absorbed by 1 c. c of a liquid at t°C is called the coefficient of absorption of the gas in the liquid at t°C.

1 c. c of water at 20°C absorbs 0.01 c. c. of carbon monoxide measured at 0°C.

1.42 litres or 1420 c. c. of water at 20°C absorb 0.01 × 1420 = 14.2 c. c. of carbon monoxide measured at 0°C.

(4) Calculate the coefficient of solubility of carbon dioxide at 5°C given that 87 c. c. of water dissolve 128 c. c. of the gas.

The gas must be reduced to normal temperature

Volume of carbon dioxide at 5°C = 128 c. c. and therefore at 0°C = $128 \times \frac{273}{273 + 5}$.

Thus we have 87 c. c. of water at 5°C absorb $128 \times \frac{273}{278}$ c. c. of carbon dioxide at 0°C.

1 c. c. of water at 5°C absorbs
 $= 128 \times \frac{273}{278} \times \frac{1}{87} = 1.45 \text{ c. c. of carbon dioxide measured at } 0^\circ\text{C.}$

The coefficient of absorption of carbon dioxide at 5°C is 1.45.

(5) Given that 92.8 c. c. of water at 15°C absorb 97.7 c. c. of carbon dioxide (measured at 15°C .). Calculate the coefficient of absorption of the gas at this temperature ... (0.998)

(6) A litre of water at 0°C is brought in contact with a mixture of nitrogen and carbon dioxide in the proportion of 1.3 vols. of the former to 7.7 vols. of the latter, the combined pressure of the gases being equal to that of 78.4 cm. of mercury. Given that the coefficient of absorption at 0°C for nitrogen is 0.0329. Calculate the volume of each gas, measured under standard conditions, which would be expelled from the water on boiling, assuming that the gases were absorbed to saturation

(350 c. c. of nitrogen; 29.0 c. c. of carbon monoxide)

(7) The coefficients of solubility of hydrogen in water and alcohol at 0°C are respectively 0.02148 and 0.06925. What must be the pressure of the gas (measured in centimetres of mercury) when the solvent is alcohol, in order that the weight of gas absorbed by a litre of alcohol at 0°C may be the same as the weight taken up by 3.42 litres of water under standard conditions of temperature and pressure? ... (806 cm. mercury.)

V Graham's Law (Rate of diffusion.)

Under definite conditions of temperature and pressure the gases diffuse inversely proportional to the square root of their densities

This is the relation that has been found out with regard to the speed with which gases move either simultaneously in opposite directions or in the same direction. It is but natural to find that a heavier body moves more slowly than the lighter one, but how much slowly is the point under consideration

As the gases in their physical properties behave similarly, the rate of the physical property also should be found to be similar and experience has proved that to be so. Thus if hydrogen and oxygen are compared then it is found that oxygen moves four times slower than hydrogen or according to the above law

the diffusion ratio $= \sqrt{\frac{1}{16}} \cdot \frac{1}{1}$ i.e. $\frac{1}{4} : 1$

i.e. $1 : 4$.

(N.B. O · H : 16 : 1)

Examples.

(1) The density of carbon dioxide relative to air, is 1·526 at S.T.P. How many cubic centimetres of air would diffuse across a given area in the same time as 125 c.c. of carbon dioxide under similar conditions.

Let V be the volume of air which would diffuse across the area in the same time as 12 c.c. of carbon dioxide, then by the formulæ

$$\frac{V}{V_1} = \sqrt{\frac{d_1}{d}} \quad [V \text{ and } d \text{ stand for the volume and the density respectively.}]$$

by substituting we get

$$\frac{V}{125} = \sqrt{\frac{1·529}{1}}$$

$$\therefore V = \frac{1259}{1} \times \frac{125}{1} \times \frac{125}{1} \\ = 155 \text{ c.c.}$$

(2) In an experiment it was found that 250 c.c. of a gas, X, diffused through a hole into vacuum in the same time as 310 c.c. of air. Calculate the relative density of air

By Graham's Law we have

$$\sqrt{\frac{\text{Density of A}}{\text{Density of air}}} = \frac{\text{Rate of diffusion of air}}{\text{Rate of diffusion of A.}}$$

$$\frac{\text{Density of A}}{\text{Density of air}} = \left(\frac{310}{250} \right)^2 \\ = 1·54,$$

i.e. the density of X relative to air is 1·54.

(3) The absolute density of nitrogen is 1·25 gm/lit. and that of hydrogen 0·09 gm/lit. Calculate the volume of nitrogen

which would diffuse through a porous membrane of given area in the same time as 100 c.c. of hydrogen. (26.8 c.c.)

(4) In an experiment the relative rates of diffusion of chlorine and hydrogen were found to be 1 : 5.99.

Given that the density of air relative to hydrogen is 14.4. Calculate the density of chlorine relative to air (2.49).

VI. Gay Lussac's Law (of combination by volumes), or the Law of Gaseous Volumes

The last thing that we have to consider about the ways in which the gases behave in a chemical reaction is about the different quantities that are required for combinations and to see if there is any general rule that governs their combinations.

Experiments have shown that when gases combine (and form compounds and not mixtures or solutions) with one another the volumes of the gases which enter into combination are very simply related to each other and to the volume of the compound produced when the latter is a gas. Hence Gay Lussac says :—

When a gas combines with another gas to form a compound and the product formed be also a gas then the ratios of the original combining gases and the gas formed are always in integer—round—numbers

Thus we have :—

2 vols. of hydrogen combine with 1 vol. of oxygen and form 2 volumes of water vapour

Similarly



Examples :—

(1) 20 litres of hydrogen are mixed with 10 litres of chlorine. Which gas remains in excess ? How many litres of hydrochloric acid gas are produced ?



$$10 \text{ litres of Cl} + 20 \text{ litres of H} = 20 \text{ litres of HCl} + 10 \text{ litres of H}$$

Thus 10 litres of hydrogen remain over in excess as they have no chlorine to combine with

(2) 60 cubic centimetres of hydrogen are exploded with 75 cubic centimetres of oxygen. Required the total volume of the gases after the explosion, measured at 150°C and 760 mm. pressure.
... (154.97 c.c.)

(3) How many litres of air at N.T.P. are required for the complete combustion of 10 gas litres of (1) marsh gas (CH_4), (2) Olefiant gas (C_2H_4) and (3) Acetylene (C_2H_2) ?

(95.23 litres, 142.8 litres; 119.04 litres.)

(4) An unknown volume of hydrogen sulphide required 110.34 cubic centimetres of chlorine for complete decomposition. What was the volume of the hydrogen sulphide ?

... (110.34 c.c.)

(5) Carbon dioxide, measuring 1800 c.c. at 10°C and 770 mm. pressure, is passed through a tube containing red hot charcoal. Any unchanged dioxide is absorbed in potash bulbs. If the latter increase in weight by 18 grams, what volume of carbon monoxide can be collected ?
(1735.2 c.c.)

(6) A mixture of nitrogen, hydrogen and carbon monoxide, 450 c.c. in volume, was exploded with an excess of oxygen 250 c.c. After the explosion the volume of gaseous products measured 500 c.c. With the removal of the aqueous vapour the volume of the product measured 400 c.c. What was the volume of each of the components in the original mixture ? A temperature of 100°C and at atmospheric pressure considered constant

(H=100 c.c., CO=300 c.c.; and N=50 c.c.)

CHAPTER VIII

Dalton's Law of Partial Pressure.

Gases as we know are so composed that there is a sufficient amount of space between different particles *i.e.* molecules ; and these molecules also have a tendency of flying away from one another. Now imagine what should happen if two substances of the above character are brought together. Naturally what we expect is, that the two kinds of the molecules of the gases, while trying to fly off from one another, will necessarily mix up among themselves so well and intimately that they would form a new substance of almost homogeneous character due to the different particles getting chances to occupy intervening spaces between the different gas molecules. Thus when two gases, which do not act chemically on one another under the conditions of the experiment, are brought together, the gases mix intimately by diffusion, so as to form a homogeneous mixture, because all gases mix in every proportion and apparently have no effect upon each other save when obvious chemical action occurs. If these mixtures of gases are subjected to different temperatures or pressures they obey the laws of Boyle and Charles as if it were a single gas. Here though there may be different gases present, yet as the gases from the point of view of the kinetic theory are made up of molecules whose physical character is simple, ought to behave in the same fashion irrespective of their individual nature, and thus must show similarity of character *i.e.* must behave as a single gas.

Thus when two gases of equal volume at the same conditions are brought together and communication made between the two vessels, it is found that the gases from the two vessels independently diffuse into one another and become uniformly

distributed throughout this double volume (the two vessels). In short each gas behaves as if it alone were present in the total space included in the two vessels. Under the new double volume of the original volume each can only exert but one-half of its original pressure.

The sum of the pressures of the two gases, however, must be again equal to unity or that much pressure which each of it originally exerted. Consequently the total pressure of a gaseous mixture may be regarded as the sum of the individual or the fractional pressures of the several components. Thus each individual component of a gaseous mixture exerts a definite individual pressure, the same that it would exert were it alone present in the container, and this individual pressure is called the 'partial pressure' of that gas.

These relations were studied by Dalton who summarised them into a statement now called the 'Dalton's Law of Partial Pressure' which is 'The pressure of a mixture of chemically indifferent gases and vapours, is equal to the sum of the pressures which each would exert, if it alone occupied the whole space.'

Thus the total pressure of air at the sea level is 760 mm. of mercury and is made up of the following partial pressures.—

Composition by volume	gas.	Composition. by pressure.
78.03 ^c	Nitrogen	587.0 mm.
20.99	Oxygen	157.6 "
1.00	Water vapour	8.0 "
0.95 ^a	Argon	7.1 "
0.03	Carbon dioxide	0.3 "
<hr/> 101.00		<hr/> 760.0

Thus it can be seen that if for instance all the oxygen were removed without change in the volume, the total pressure would be 760.0 — 157.6 = 602.4 mm. Similarly if the water vapour were removed instead of oxygen the pressure would be 760.0—

$8\cdot0 = 752\cdot0$ mm. Thus it is evident from the law of Boyle that if the pressure had been maintained constant at $760\cdot0$ mm. and a portion of the mixture say water vapour was removed then the volume would have to decrease to $\frac{752}{760}$ of its original volume. The application of this principle is important when a gas has been measured over water, because in such a case the volume of the gas is not the true volume of the gas alone but is due to the gas plus the water vapour. That is when aqueous vapour is present in a volume of a gas we have again the consideration of a gaseous mixture.

The partial pressure of water vapour in a gas in contact with water is independent of the total pressure of the gas and varies only with the temperature.

Examples

(1) If 100 vols. of air consist of 20.66 oxygen, 77.9 nitrogen, 0.03 carbon dioxide, and 1.40 of aqueous vapour, and the barometer stands at 760 mm. What is the partial pressure of each of these gases and vapours?

$$(O = 157\cdot01 \text{ mm.}, N = 592\cdot11 \text{ mm.}, CO_2 = 0\cdot23 \text{ mm.}, \\ H_2O = 10\cdot6 \text{ mm.})$$

(2) A mixture of equal volumes of dry oxygen and nitrogen is collected over water at $750\cdot2$ mm. Calculate the partial pressure of the gases in the mixture neglecting the water vapour.

(3) The following quantities of gases are contained over mercury in separate measuring vessels —

- 70.0 c.c. of hydrogen at $15^\circ C$ and 720 mm.
- 10.0 c.c. of oxygen at $10^\circ C$ and 700 mm.
- 14.0 c.c. of nitrogen at $30^\circ C$ and 760 mm.

* All are mixed in another vessel at $18^\circ C$ and the volume is found to be 94.00 c.c. What is the total pressure in the vessel and the partial pressure of each constituent?

(731.0 mm. Total, 54.7 mm. H, 77 mm. O; and 112 mm. N)

CHAPTER. IX.

The Kinetic Theory of Gases.

All gases irrespective of their nature *i. e.* whether a simple gas, a gaseous compound or a mixture of gases, and also whether an active body like chlorine or an inactive body like nitrogen, (these all) behave identically in almost all of their physical properties. We have already seen that the laws of Boyle, Charles, Henry, Graham and Dalton are all equally obeyed implicitly by the different gases. From this it becomes quite obvious that as they have similarity of behaviour they also must have similarity of constitution or rather similarity of composition.

To account for the gas laws and also the departure from these laws which are also almost of universal character it seems to point to an equally simple and universal constitution for all gases.

It is but natural to consider whether any mental picture of the nature of gases can be suggested which can serve to account for the simple laws which have been found to represent their behaviour, and also to account for the deviations from these laws. Such a mechanical representation was brought by Bernoulli as far back as 1738 and has been developed by later workers into the "Kinetic Theory of Gases."

The first fact to arrest attention is the expansive tendency, causing gases to fill, with uniform concentration, any space within which they may be liberated. This can easily be explained from the following considerations *i. e.* the Kinetic Theory. According to this Kinetic Theory, (Kineo = I move), gases are made up of small perfectly elastic particles—the chemical molecules—which are in continual rapid motion,

colliding with each other and with the walls of the vessel containing them. The particles of any one gas are supposed to be identical, but differ from the particles of other gases in respect of mass, speed and other properties. The space actually filled by the gas particles is supposed to be smaller than that which they inhabit under ordinary conditions. They have therefore a comparatively large free space in which to move, and are practically free from each others influence except during a collision. The average distance over which a particle moves before colliding with another particle is termed the Mean Free Path of the particle.

In the course of their movement, molecules must be continually striking on and rebounding from the walls of the containing vessel, thus exerting a certain pressure which obviously will be all the greater, the greater the number, mass and velocity of the colliding molecules.

Thus to put the above idea in a more systematic form it would be:

- (1) Gases are made up of minute particles *viz.* molecules which are in continual rapid motion colliding with each other and with the walls of the containing vessel.
- (2). The molecules are perfectly elastic, smooth and spherical.
- (3). The volume actually occupied by the gas molecules is small compared with the volume the gas occupies under ordinary conditions.
- (4). The gas molecules exert a slight attractive force.
- (5). The molecules are infinite in number.

Now let us examine each clause separately

The first clause assumes that molecules are in continual motion. Why? The phenomenon of diffusion leads us to assume that molecules must be in rapid motion. The gases cannot diffuse one into the other if molecules are at rest. Further

if molecules are at rest a mixture of two gases on standing will show signs of settling into two constituents due to difference in specific gravity, but mixture shows no signs of settling and hence the diffusion and absence of settling in a mixture of gases leads us to assume that molecules must be in continual motion. Further clause (1) accounts for the pressure exerted by the gas. It is clear that a pressure is exerted on the sides of the containing vessel every time a molecule strikes the boundary wall. Hence clause (1) of the Kinetic Theory accounts for diffusion of gases and the pressure exerted by a gas when confined in a vessel.

Clause (2) describes the molecules of a gas. It assumes the molecules to be perfectly elastic. If the molecules are not elastic, then, after a collision, they will not rebound with the same velocity as before, and the velocity after every collision will decrease and ultimately will become zero when the gas will cease exerting the pressure. This is contrary to experience and hence the molecules must be perfectly elastic.

The molecules are further assumed to be perfectly smooth *i. e.* frictionless for otherwise after every collision due to friction the velocity will diminish and ultimately become zero when the gas will cease exerting the pressure. This being impossible, the molecules must be perfectly smooth.

Lastly clause (2) assumes molecules to be spherical. The spherical shape is assumed because as a general rule we find that rotating and revolving bodies in nature assume spherical shape. Our Earth and the planets which revolve round the Sun are known to be spherical bodies. Hence molecules which are in continual motion are likewise assumed to be spheres.

Hence clause (2) of the theory gives us a general conception of the molecules.

Clause (3) accounts for the compressibility of gases. 'It states that there is a free space between molecules and hence on applying pressure the volume diminishes due to crowding together of molecules'. The clause introduces the concept of Mean Free Path of a molecule since there is a large free space

between the molecules, a molecule has to move over a certain distance before it can collide with another molecule. This distance is called the M.F.P. of a molecule. Hence clause (3) accounts for the compressibility of a gas and introduces the concept of M. F. P. of a molecule.

Clause (4) accounts for the deviation of gases from gas laws

Thus according to this theory the pressure exerted by a gas, or its elastic force on the walls of the containing vessel, is due to the combined effect of the bombardment of its molecules against the walls of the vessel. It is quite evident, therefore, that the magnitude of the pressure must depend upon the mass and the velocity of the particles. It can be shown that the pressure exerted by a single particle is proportional to its mass and to the square of its velocity, and the total pressure is the sum of the pressures exerted by each of the particles

Thus to put it in a mathematical form it would be

If " n " be the number of molecules of mass " m " each, be present in a volume " v " at pressure " p " and if " c " be the velocity with which each molecule moves, then $pv = \frac{1}{3} m n c^2$ (Kinetic Equation)

Now it can easily be seen that the simple gas laws are in full accord with the view as to the constitution of gases just stated. If at constant temperature the volume in which a definite mass of a gas is confined, is halved, the number of impacts, on the walls in a given time, is doubled, in other words, the pressure of the gas is doubled, and this is Boyle's Law of Gases

Further we have already seen that at constant volume the pressure of a given mass is proportional to the absolute temperature. As increase of temperature cannot alter the number of particles, the observed increase of pressure, must according to the kinetic theory be due to an increase in the speed of the particles, resulting in a greater number of impacts on the walls of the vessel in a given time.

Further again we have seen that mechanical considerations show that two swarms of moving particles such as according to

the kinetic hypothesis, gases are supposed to be and are in equilibrium with each other, when the average kinetic energy of their particles is the same. Now real gases are actually in equilibrium when under the same temperature and pressure, i. e. they can be mixed without pressure or temperature undergoing any alteration. Hence if the actual constitution of real gases is truly represented by the kinetic hypothesis, equal volumes of different gases, at the same temperature and pressure, must possess equal amounts of molecular kinetic energy. Thus two equal volumes of different gases under the same conditions of temperature and pressure, exert the same elastic force i. e. pressure, upon the containing vessel, that is to say, the kinetic energy in each volume is the same. According to Avogadro's hypothesis (still to be explained) equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules, however much the weight of these molecules may vary; therefore the average kinetic energy of each individual molecule will be the same. It follows from this that the mean velocities of the different molecules must vary, and the calculated numbers representing the actual velocities of movements of the molecules of different gases show that, these rates are proportional inversely to the square root of their respective densities. But according to the law of gaseous diffusion (Graham's law) the relative rapidity of diffusion of gases is inversely proportional to the square roots of their densities. Hence by a purely mathematical process, based upon the kinetic theory of gases, the law of gaseous diffusion is proved to be true. Similarly the kinetic theory could be seen to be applicable to the phenomena of condensation, evaporation, solution etc.

Thus again to put the above considerations in mathematical forms

I Boyle's law of gases

Boyle's law can also be deduced from the Kinetic Equation given above. The right hand side of the equation is made up of factors which are cast up at constant temperature. It follows, therefore that at constant temperature the product of pressure and volume equals a constant, which is Boyle's law

$$c = \sqrt{\frac{3 RT}{\text{constant} \times d}}$$

∴ if temperature T is constant,

then $c = \text{constant} \times \sqrt{1/d}$ or $c \times \sqrt{d} = \text{constant}$, so that the velocity with which a gas molecule moves is inversely proportional to $\sqrt{\text{density}}$ at constant temperature

Since diffusion is due to the molecular velocity it follows that at constant temperature the rate of diffusion is inversely proportional to $\sqrt{\text{velocity}}$ which is Graham's law of diffusion

Having deduced the gas laws we will now proceed to point out the importance of the Kinetic Theory.

- (1) First of all the Theory gives a satisfactory explanation for the laws followed by the gases
- (2) The Theory enables us to calculate the speed at which the molecules move.

According to the K. E.

$$C = \sqrt{\frac{3 p v}{m n}}$$

Hence substituting the known values on the right hand side of the equation the value for the speed can be calculated.

- (3) It explains the phenomena of condensation and evaporation ; thus

We know that the different particles in a liquid have not the same freedom of movement as in a gas, although they may be assumed to be identical with the gaseous molecules and have equal velocities. On account of this difference in the freedom of independence the molecules in a liquid though do not move as freely as in a gas, still they have sufficient freedom and move quite freely within the liquid itself and thus under the influence of gravitation accommodate themselves to the shape of the vessel containing the liquid. In spite of the clinging together of the molecules in a liquid still during their movement those that are near the surface have sufficient motion to free themselves from their neighbours and leave the liquid altogether and become free

gas molecules Now if these molecules travel unhindered the space made vacant by them will be taken up by other similar molecules from the liquid and this will go on till all the liquid is evaporated But if the liquid is kept in a closed vessel then the shooting gas molecules will travel only up to the walls of the container and will of necessity travel backwards and thus return to the liquid and be retained by it : *e.* again the gas will be condensed and so the cycle will continue and a state of equilibrium will be reached when the number of molecules going out and coming in become equal.

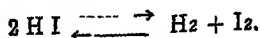
(4) It explains the phenomenon of solution.

When a soluble crystalline substance is brought in contact with the solvent, some of its particles become detached and enter the solvent and then move freely in the solvent After a time these moving particles come again in contact with the solid and are retained by it. This give and take process goes on untill the number of particles proceeding from the solid and coming to the solid is the same in a given time. No further apparent change takes place and the solution is said to be saturated

(5) It explains the phenomenon of thermal dissociation

According to this theory the molecules of a gas are constantly in motion Although we assume a constant mean-velocity for the molecules as a whole body still the velocities of the individual molecules must be considerably different because of their frequent collisions with one another. And thus as the velocities are different they will arise at different temperatures such conditions that atleast some will have their velocities far greater than their mutual attraction Now it is very easy to conceive that under such circumstances the velocities at last may become so violent as to throw the molecules or atoms out of their space of mutual attraction The molecule is thus broken or decomposed This will however occur only with those molecules whose velocity is above a certain limit Thus we can easily see why a partial decomposition takes place The explanation for

partial combination is exactly the same and thus we can see why there is a state of dissociation in a gaseous body like hydrogen iodide.



From the explanations and results got above, we may fairly conclude that the mechanical structure postulated by the kinetic hypothesis, as far as we have gone, is an accurate model of that actually possessed by existing gases.

Upto this point, the tacit assumption has been made that the particles constituting the ideal gas are mere points and are without any mutual attraction or repulsion and are even incompressible. The diminution in the volume on compressing a gas is ascribed entirely to a diminution in the free space between the particles; or in other words, we have, in the first broad survey of the question neglected to consider what effects their size etc., would produce.

Even taking into consideration the above facts about the size, attraction, compressibility etc., of the molecules which are bound to bring in, deviations of the laws, still the kinetic theory not only accounts satisfactorily for the obedience to the laws, but also for the fact that the deviations from the gas laws are the smaller the lower the pressure. Under these circumstances, the attraction between the particles becomes negligible owing to their distance apart, and the volume of the particles is negligible in comparison with the total volume.

It may be seen thus that no actual gas behaves exactly according to the simple gas laws, but the deviations in the case of hydrogen, helium, nitrogen, and other gases which are difficult to liquefy, are very slight at ordinary temperatures and pressures. A gas which would follow the gas laws accurately is termed a perfect or an ideal gas.

Thus Kinetic Theory expresses the modern views of the physicists concerning matter in the gaseous state and serves to harmonize and explain the physical laws relating to the properties

of gases. The following points regarding it are worth remembering —

(1) All gases seem to have the same mechanical structure, as they respond in the same way to changes of energy, such as those of temperature and pressure.

(2) Gases cannot be in any sense a continuous matter, but must be extremely porous, as they are always very compressible, and also tend to expand indefinitely.

(3) The pressure that is exerted by gases cannot be the thrust of a rigid body, as that of a spring, and thus under the circumstances, almost the only way in which we can imagine the application of pressure is by the momentum of the moving bodies. Hence we may imagine a gas to be made up of moving particles whose aggregate impact is the cause of the pressure exerted upon the walls of the containing vessel.

(4) According to Boyle's law the volume of a gas is reduced to one half when the pressure is doubled. This is in accord with the picture that we have drawn, for in the half volume the particles will strike the walls of the container twice as often and thus exert twice the force on the same area in a given time.

(5) From the corollary of the law of Charles we know that rise of temperature increases the pressure, which must be due in some way to the increase of the kinetic energy of the moving particles. This might be brought about by increasing either the mass or the speed of the particles, for then the kinetic energy is equal to the expression $\frac{1}{2}mv^2$ in which 'm' represents the mass, and 'v' the speed. Experiments have shown that the mass of a gas is not changed by heat. Hence it must be nothing else but the speed of the particles that is affected.

(6) The pressure of all gases increases equally for equal rise in temperature; so the aggregate energy of the various kinds of gas particles must increase to the same degree. Now it can easily be shown that the masses of particles of two

different kinds of gases are different. Hence the speed of the particles must be increased—or decreased inversely as the square root of their mass, in order that the $\frac{1}{2}mv^2$ may be increased—or decreased—for two different particles.

(7) All the facts about diffusion are quite in keeping with the idea that the gases are made up of moving particles and Graham's law, which states that the rate of diffusion is inversely proportional to the square root of the density of a gas, is but another way of stating the conclusions of the preceding idea.

(8) The expansive tendency of gases, causing them to fill with uniform concentration, any space within which they may be liberated is due, according to the picture drawn, to the gas molecules being, on the average, far apart relative to their own size, and also in rapid motion. Thus as soon as a free space is offered to the gas, molecules already moving in that direction pass in, and in virtue of the continual movement, the average number of molecules per cubic centimetre speedily become the same throughout.

(9) Finally our picture becomes clearer and clearer and more harmonious if we assume that, in equal volumes of all gases there is the same number of particles.

Summary of the kinetic theory. In conclusion we might say that as a picture, which gives a graphic representation of the simple conduct of the gases, the kinetic theory suggests that :—

- (1) All gases are made up of small particles (molecules) relatively apart and in continual motion.
- (2) Equal volumes of all gases, contain the same number of particles (molecules) whose momentum is the cause of pressure.
- (3) The kinetic energy of all the particles (molecules) is increased equally by a given rise in temperature, the increase being due to the increased speed of the particles

A. D. Risteen has compared the results of observation with the deduction from the kinetic theory. Some of them are as follows.—

Results of the theory.	Results of observation
(1) The molecules of a gas are all alike	(1) Gases are homogeneous and show no signs of settling, nor can the molecules of <i>any particular gas</i> in general be separated, by diffusion into different molecules (A special case—dissociation—is different) Gases have also many physical properties in common
(2) Molecules are at relatively great distances apart and in constant motion in straight lines.	(2) The compressibility, permeability and diffusivity of gases is very great The incompressibility of gases at high pressures is supposed to be due to the abnormal crowding of the molecules
(3) In a given mass of molecules, the product pv is proportional to the average kinetic energy per molecule	(3) In a given mass of a gas the product pv is proportional to the absolute temperature, &c This includes the laws of Boyle, Dalton and Charles.
(4) Diffusion	(4) Graham's law
(5) The average kinetic energy is constant for every set of molecules in a mixture of gases	(5) So far as we can tell, the temperature of each constituent of a mixture of gases is the same
(6) If two sets of molecules have the same kinetic energy and the same pressure they contain the same number of molecules per unit volume	(6) Avogadro's hypothesis, and the law of (Gay) Lussac

CHAPTER. X. _

The Three States of Matter.

Every substance can be made to exist in any of the three physical states, solid, liquid and gaseous, of itself. The individual physical state depends upon the temperature and pressure to which the substance is subjected. These three different states are mutually interconvertible without any residue.

I. Relation between Liquids and Gases.

(a) **Evaporation.** When a liquid like water is kept in an open vessel exposed to air, we find that it gradually disappears or rather gradually passes into the air, and this process is called evaporation. (e = out, and vapor = vapour). There is no definite temperature at which a liquid passes into vapour or gas. It does so at all temperatures. If the liquid is kept in a partially filled closed vessel then the liquid does evaporate, but this goes on till the empty space gets saturated with the vapour of the liquid. (Speed of particles escaping and entering equalises. If the temperature is increased then the speed increases, and thus the amount of vapour also increases.)

(b) **Vapour pressure.** When a liquid is evaporating it gives rise to new particles—vapour of the liquid—which are all flying about, and as they are gas particles they exert a pressure on the liquid and on the vessel as well. This pressure due to the vapour is called the pressure of the vapour or better 'Vapour Pressure' and is generally restricted to water vapour only. If reference is only to be meant for water vapour then, this is expressed also by different terms (α) Relative Humidity or (β) Aqueous Tension.

(α) **Relative humidity** means the quantity of water present as compared with the quantity that would be present if saturation takes place at the same temperature

(B) **Aqueous tension** The amount of vapour present can be expressed also by other method, and that is from the pressure it exerts on the surroundings. And from this vapour pressure may be defined as "The pressure upon its surface (water) due to its own vapour"

This formation of vapour brings about an accidental inaccuracy in the calculation of the gas volumes collected over water; because if gases are collected over water then some water must change into vapour. This vapour then occupies the gas-holding space together with the prepared gas. Hence if the volume of the gas is to be measured accurately then the space occupied by the vapours of water must be subtracted from the gas volume. This can be calculated from the law of partial pressure. Thus

Suppose at temperature 20°C the vapour pressure of V.P. is 17.4 mm and the total pressure of the air is 760 mm then 17.4 and 742.6 ($760 - 17.4 = 742.6$) will be the vapour pressure and air pressure respectively. Therefore the total volume of water in the air is according to the ratio $\frac{17.4}{760}$ of the total volume. Now if this volume is taken for the sake of argument, say 1,000 c. c. then the total amount of water vapour in these 1,000 c. c. will be $\frac{17.4}{760} \times 1,000 = 22.189$ c. c.

But instead of deducting the volume like the above, it is more convenient to deduct the whole vapour pressure from the air pressure if the gas is to be reduced to N.T.P., because the idea is to get rid of any accidental conditions and hence the formula for reduction of a gas volume to N.T.P. becomes —

$$V = \frac{V \times (P - a)}{760 \times t}$$

Examples

(1) 79.3 c. c. of air are measured over water at 11°C . and 753 mm. What would be the volume dry at N.T.P.? The vapour pressure of water at 11°C is 10 mm

The pressure of dry air therefore at 11°C is :—

$$753 \text{ mm.} - 10 \text{ mm.} = 743 \text{ mm}$$

∴ The actual volume is .—

$$\frac{743 \times 273 \times 79.3}{760 \times (273 + 11)} = 74.5 \text{ c. c.}$$

(2) 170 c. c of a gas are measured over water at 15°C and 720 mm. What will be the volume dry at N.T.P.? The vapour pressure at 15°C is 12.7 mm (150 c. c.)

(3) 27.3 c. c of oxygen are measured in a dry eudiometer over mercury at 0°C and 367 mm. The gas was transferred to a vessel standing over water and the water was brought to the same level inside and outside the vessel. What volume would the gas occupy at 27°C and 760 mm.? V P at 27°C = 26.5 mm. (150 c. c.)

DENSITY OF GASES.

By the density or absolute density of a substance is meant the number of units of mass of the substance which occupy unit space. The standards for mass and space are a gram and a cubic centimeter, and thus the density of any substance is the number of grams of that substance which occupy one cubic centimeter. We already know that substances—solids or liquids or gases—are all affected by the change of temperature and their volumes change for the same quantity or the number of grams. Thus the density of one and the same substance would be different at different temperatures, and this is very marked one in the case of gases.

In the cases of solids and liquids the changes involved in the volumes by alterations of temperature vary very widely and that too in a very irregular manner. But for the gases we have already seen (cf Boyle's law and Charles's law) that the amount of expansion or contraction produced by raising or lowering of the temperatures is practically the same for all of them through the same alterations.

Hence it follows that the relative density of a solid or a liquid may vary with the temperature or pressure, since the effect of change in these factors upon the volume of a substance and upon that of the standard chosen may not be the same. The relative density of a gas is, however, constant, since changes in these factors affect all gases alike.

The relative densities of gases are of rather great importance in chemical theory. The standard chosen in these measurements is not "1 c. c. of water at 4°C", but is altogether a different one and it is a gas. Sometimes it is air and more often it is hydrogen as it is the lightest of all known gases.

The weight of 1 c. c. of hydrogen at standard conditions of temperature and pressure i. e. N.T.P is 0.0000899, and that of oxygen is 0.00143. Similarly other gases give also very inconveniently small numbers, for the relative densities of gases if these were uniformly compared with water at 4°C as standard. So for this and other reasons the densities of gases are expressed in other units than those of solids and liquids as seen above. An important distinction between this standard and that adopted for the comparison of relative densities of liquids and solids is that it is not the standard at any particular temperature and pressure for reasons already referred to. It is not therefore at all necessary to compare the relative densities of other gases with the density of hydrogen under any particular conditions of temperature and pressure, but it is sufficient to have them only under the same conditions. Thus -

The specific gravity or relative density of a gas or vapour is the ratio of its mass to the mass of an equal volume of hydro. gen measured at the same temperature and pressure

The relative density of a gas is commonly termed density of the gas and the relative density of the vapour of any substance, the vapour density of the substance.

One gram of hydrogen under standard conditions measures 11.1636 litres. This volume is a convenient volume for

measuring densities and using this unit, the densities are expressed by the same numbers as the relative densities or specific gravities, but often times this one gram is found to be too large a mass for convenience and thus the practice now adopted is :

The litre is taken as the unit of volume and the mass of a litre of normal hydrogen called a crith = 0.896 grams is taken as the unit mass. Thus -

The density of a gas is the number of criths contained in one litre of it at 0°C and 760 mm., or the number of times it is heavier than an equal volume of hydrogen.

(a) In case the density of a gas is expressed as compared to air, then to find the density referred to hydrogen, multiply the given number by 14.436 (density of air referred to hydrogen) and you get the density referred to hydrogen.

Thus sulphur dioxide is 2.22 times heavier than air, what is its density referred to hydrogen ?

$$2.22 \times 14.436 = 32.04 \text{ the density of sulphur dioxide as referred to hydrogen}$$

(b) To find the mass of a litre of gas the density of which referred to air is given, multiply the mass in grams of a litre of air by 1.293

Thus carbon dioxide is 1.529 times as heavy as air, what does one litre of it weigh ?

$$1.529 \times 1.293 = 1.977 \text{ gram.}$$

(c) To find the density referred to air from that referred to hydrogen, multiply the density of hydrogen referred to air by 0.06926

How many times is nitric oxide ($\text{NO} = 30$) heavier than air ? The density referred to hydrogen is 15.

$$0.06926 \times 15 = 1.0389 \text{ density referred to air.}$$

Examples .

(1) Given that one gram of hydrogen occupies 11.1 litres, and that 526 cubic centimetres of air weigh 0.6786 grams

Calculate the specific gravity of air in terms of the hydrogen standard. ..(14'35)

(2) The calculated relative density of chlorine ($H=1$) is 35'23. What is the relative density of the gas referred to hydrogen? ..(2'216)

(3) What is the relative density of hydrogen chloride (mol. wt = 36.47) referred to hydrogen, air, oxygen and chlorine? .. [

18.05 ($H=1$), 1.259 (air=1), 1.139 ($O=1$), 0.514 ($Cl=1$).]

(4) A gas with the relative density 15 ($O=1$) was reduced from the standard conditions to $20^{\circ}C$ and 740 mm. pressure, so that it might have a volume measuring 6172.3 c.c. What is the weight of this volume of the gas? (12 grams)

(5) Given that the absolute density of air is 0.001293 gram per centimetre, and that the relative density of carbon dioxide referred to air as standard is 1.529. Calculate the volume in litres which would be occupied by 100 grams of carbon dioxide. (50.59 litres).

(6) The specific gravity of coal gas is about 0.5 referred to air as unity, and air is 14.435 times heavier than hydrogen. Calculate from these data the weight of coal gas at $10^{\circ}C$ and 530 mm pressure, required to fill a balloon having a capacity of 800 Cu m. . (347.96 kilograms).

(7) 41.6 c.c. of hydrogen saturated with moisture were confined in a glass tube over mercury at a temperature of $16^{\circ}C$. The distance from the closed end of the tube to the surface of the mercury inside the tube was 386 mm and to the surface of the mercury outside the tube 491 mm. Given that the atmospheric pressure was 740 mm of mercury. Calculate the volume of dry hydrogen under standard conditions

Vapour pressure of water at $16^{\circ}C=13.5$ mm. . (32.1 c.c.)

(8) 10 grams of a gas, measured at $-48^{\circ}C$ and 600 mm. pressure, were expanded by heating to $177^{\circ}C$ and reducing the pressure to 480 mm. Of the rarefied gas 250 c.c. weighed 0.5

gram. What was the original volume of the gas, and what was the density of the gas at its original and final volume ?

... (Original density = 5 ; Final density = 2).

Boiling Point. When heat is imparted to a liquid, some of the heat energy goes to raise the temperature and some to change the liquid into vapour (latent heat of vaporization). This vapour standing over the liquid imparts a certain pressure on the atmosphere above, which in turn tries to push it down. But when heating is continued to the extent of equalizing the atmospheric pressure, then all the heat energy goes to change the liquid into its vapour, and the temperature remains constant. This temperature for that pressure is called the 'boiling point' of that liquid, and may be defined as the temperature where the vapour pressure is equal to, or better just overcomes the pressure of the atmosphere above it.

The boiling point is usually indicated by the rise of bubbles in the liquid and this is an accurate test. Because suppose a bubble of water is formed at 'A' fig 7.

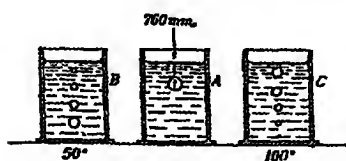


Fig. 7

The pressure upon the bubble will be 760 mm. plus that of the water layers. In order that the bubble may survive, the vapour pressure must exceed the opposing pressure. A bubble while forming at 50°C in 'B', when travelling up will collapse on account of the vapour pressure (the gas bubble) being insufficient to overcome the pressure of the layers of water and the atmospheric pressure, and also on account of the contraction due to the lower temperature of the upper layers. But at 'C' at 100°C the vapour pressure of the bubble exceeds the external pressure. It is not cooled as it rises but increases in size as the pressure diminishes and finally escapes from the surface.

Critical Temperature . At high temperatures gases may be subjected to the greatest possible pressure, and still (though Boyle's law requires) they will not contract enough and pass into the liquid state. As for instance suppose we take a small, stout sealed glass tube nearly full of liquid water. If this is gradually heated to a temperature between 350°C and 400°C , the surface of the liquid water will grow more and more indistinct and will ultimately vanish, complete vapourization having apparently occurred. But on slowly cooling, a mist suddenly appears about the middle of what has looked like an empty tube. This rapidly spreads and then *suddenly* a quantity of liquid water (vanished) becomes visible in the lower part of the tube.

Here it is quite apparent that the pressure in the tube when heated, by Charles's law, must be very high and the above behaviour of water -going into vapour- shows that no pressure however great is able to retain water in the liquid (state) form above a certain temperature and this temperature is aptly called the 'Critical temperature or 'Critical point'

Thus Critical temperature is that limit of temperature for a gas (different gases have these limits quite different) below which the gas must be cooled before it can be liquefied by subjecting it to any pressure, however great

The behaviour of critical phenomenon is common to all the gases- or liquids. The pressure required to cause liquefaction at the critical temperature is called the "Critical Pressure". The critical pressure is not generally more than sixty atmospheres, and if hundred atmospheres pressure does not liquefy a gas, then it is useless to increase the pressure, a lower temperature being the necessary condition.

II. Relation between Solids and Liquids

The majority of liquids when they are cooled sufficiently then reach a temperature at which a sudden change begins, and the liquid generally freezes to a mass of crystals and the temperature remains constant. Some liquids, such as wax, glass

and glue have no definite points of solidification, but get more and more viscid, and ultimately assume a hard mass of apparently solid condition.

When substances assume solid condition from the liquid state, then all the substances necessarily do not have well formed particles, but some solidify into particles—grains—without any regularity or order and thus present no definite external shape or form. Thus we have solids of two kinds : (1) **Crystalline** (Kryos = frost), and (2) **Amorphous** (a = not ; morphe = form), or non-crystalline.

Crystalline substances have a definite point of solidification, while the non-crystalline otherwise called amorphous have as a rule no definite point of solidification.

Melting point. When a crystalline solid is slowly heated the temperature rises to a certain definite point. Further application of heat does not raise the temperature, but the solid changes its state and becomes liquefied. The energy applied now completely being spent in change of condition, solid to liquid and this point of temperature is called the melting point of the solid, of course the pressure here is taken for granted to be remaining throughout constant.

Freezing point: When a liquid is slowly cooled down, then the converse of the above one ought to take place, but sometimes it does not, and so a liquid does not necessarily crystallize at its melting point, but may be undercooled. "Freezing-point" is therefore a temperature at which both the solid and the liquid may remain unchanged in contact with each other.

If the undercooled solution is either disturbed or a crystal of the substance is thrown in, then the liquid suddenly changes its liquid state into the solid one, without any quantity whatsoever of the liquid remaining behind unchanged. Such point—of temperature—where a liquid solidifies is called its point of 'solidification.'

In solidification heat is given out and in both the cases the energy change opposes the physical change taking place.

Vapour pressure of solids. Many solids give off vapour at ordinary temperatures just as liquids do. This is evident from the odour of things like camphor or naphthalene or musk etc. When such solids are heated (slowly) the vapour pressure increases in value and when it increases to the point, where it exceeds the pressure of the atmosphere, then the solid passes directly into a gas without melting or getting into liquid state and then boiling. When the vapours of such substances are again cooled down they directly pass into the solid form without the intermediate liquid state. The process of converting a solid directly into its vapour without the intermediate liquid state and cooling the vapour into a solid state again is called "Sublimation", and the collected solid is called the 'Sublimate.'

Crystallography.

Crystals. From what has been discussed so far, we can gather that substances assume solid form—according to their individual nature—and are either crystalline or non-crystalline : *i.e.* amorphous. Similarly we have seen that these solids, especially crystals, can be had either from —

- (a) Liquids freezing into solids.
- (b) Vapours condensing *i.e.* either by sublimation or otherwise.
- (c) Solutions of the solids.

When a fluid freezes (or solution throws out a solid) to a solid it usually changes into a mass of solid bodies each of which has a definite (having fixed limits, bounded with precision) geometrical form, then these are called crystals. These crystals are bounded by plane surfaces which are arranged in an orderly fashion with reference to imaginary lines drawn through the crystals, called the axes.

Thus every crystal has a definite geometrical form and the variety of crystals may be endless. Still they may be classed into one of the six systems arranged with reference to the angles which the axes subtend at their point of intersection.

Thus :—

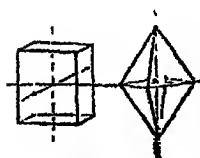
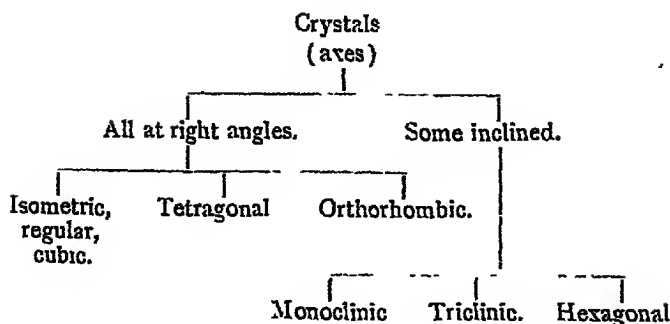


Fig 8

(1) Isometric or *Regular* or *Cubic* (iso = equal, metron = measure) system is one which has three equal axes, and these all are at right angles to each other.

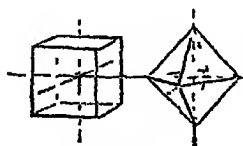


Fig 9

(2) Tetragonal (tetra = four; gonia = angles, or having four sides) is that system in which all the axes though at right angles still two of them are equal and the third is of a different length than the other two

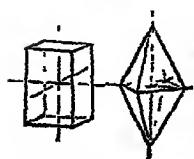


Fig 10

(3) Orthorhombic (Ortho = straight, simple; and rhombus = quadrilateral.) system is one in which though the angles of intersection between the axes are all right angles still the sides are all unequal.

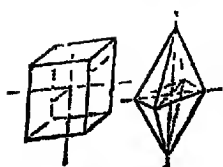


Fig. 11

(4) **Monoclinic** (Monos=single, clin=to bend.) is a class which has two axes at right angles, and a third at right angles to one and inclined to the other. The length of the axes is any and the inclination of the angles varying from 0° to 90° .

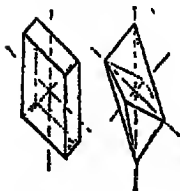


Fig. 12

(5) **Triclinic** or Asymmetrical system has all the three axes inclined to each other, and the angles and the lengths of axes all varying.

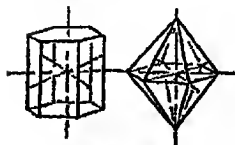


Fig. 13

(6) **Hexagonal** system has three equal axes in the same plane intersecting at an angle of 60° and the fourth one at right angles to all these.

Crystals are also arranged according to their hardness and this hardness is classified into ten varieties

Scale of hardness of minerals.

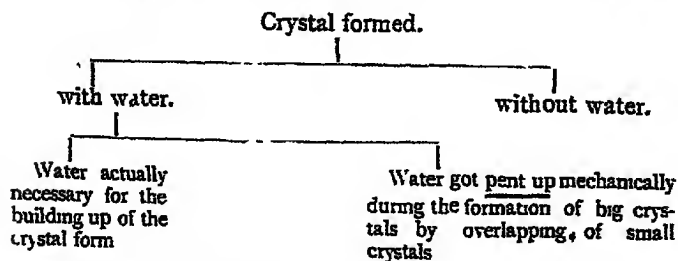
- | | |
|----------------|----------------|
| 1. Talc. | 6. Orthoclase. |
| 2. Selenite. | 7. Quartz |
| 3. Calcite. | 8. Topaz |
| 4. Fluor spar. | 9. Corundum. |
| 5. Apatite | 10. Diamond. |

Talc is the softest and diamond is the hardest variety of the above, and these different grades are called "Degrees of Hardness."

Behaviour of the crystals. All crystalline substances do not show the same fixity of form and good many of them change their normal state, of course due to extraneous

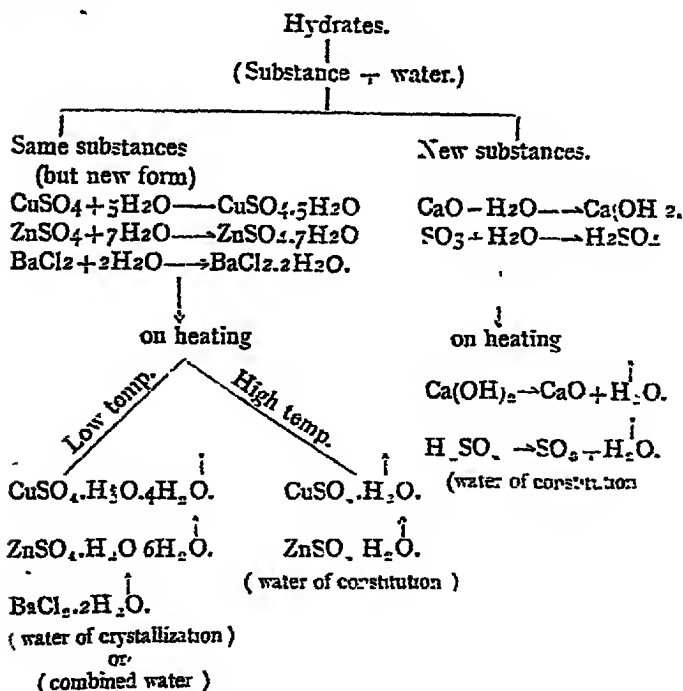
conditions. Thus crystals may become moist like those of crude common salt, or crumble down to powder like those of washing soda or glauber salt. This phenomenon is due to the difference in the amount of moisture *i. e.* relative humidity in the air. If the water *i. e.* water vapour pressure in the atmosphere is greater than is required for mutual equilibrium (*i. e.* between the water vapour of the crystals and that of the atmosphere) the salt will keep on absorbing moisture, and if less, will keep on giving out the required quantity till equilibrium is established. When the crystals absorb moisture and become moist then this is called "Deliquescence" (*de* and *liquesco*=melt), and when the crystals give out water from their bodies, and crumble to powder or atleast become opaque then it is called "Efflorescence" (*ef* for *ex*, and *floresco* from *floreo*=to blossom).

From the above behaviour of crystals we might be led to think that all crystalline substances contain water but it is not so always. The majority of minerals e. g. diamond, quartz, are crystalline without any water. Similarly common salt is a body that requires no water for the building up of the crystalline structure. Thus crystals may be formed with water and without water.



The water that is necessary for the building up of the crystal is called the "water of crystallization", and as here there is a combination of water molecules with the molecules of the substance the same water of crystallization can be styled as "water of hydration" as the above substance is a hydrate.

The crystals when formed are formed with a fixed number of molecules of water of crystallization e. g. in copper sulphate there are five molecules of water i. e. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Now if the crystalline copper sulphate is heated, we expect to drive away all the water and get only copper sulphate CuSO_4 . But what really happens is that upto $100^\circ - 110^\circ$ only four molecules of water are lost and the fifth one persists in holding on to the copper salt, and if stronger means i. e. higher temperature say 210°C , is applied then the fifth molecule of water does go away, but at the same time brings about the decomposition of the copper sulphate; and as this decomposition makes copper sulphate lose its original constitution, this water is appropriately called "water of constitution." Thus :



Thus we may have :—

- (1) Water of hydration.
- (2) Water of crystallization or combined water.
- (3) Water of constitution.

(1) Water (molecules of) that makes a substance assume a definite crystalline form is called the water of crystallization. When the water is removed the crystal usually crumbles to original power or amorphous condition (as all crystals containing water of crystallization necessarily do not have the water of constitution).

(2) Water (molecules of) that, so to say forms a part and parcel of the molecules of compounds, makes the nature—chemical—of the compounds change, when this is removed from them, is called “water of constitution.” This may be of two types .—

(i) When water is added to burnt lime CaO , a new compound the hydroxide Ca(OH)_2 is formed. Here the addition of water has produced an essentially different compound. If this hydroxide is again heated we again find that the hydroxide *i. e.* a base changes into an oxide, a compound of a different type altogether.

(ii) When copper sulphate (or similar crystals) is heated between 100°C to 110°C then it loses only four molecules of water out of five and its formula for the remaining compound may be written as $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}$). To drive away the last molecule of water a much higher temperature is needed, in fact a temperature of about 210°C . But at this temperature the salt itself begins to undergo decomposition, and chemists have agreed to call this water which is thus

more closely bound to the salt, water of constitution, whilst the other portion which is usually driven off at 100°C is called water of crystallization

(3) When water as such is simply taken up and forms an additive product (and not substitution) like the water of crystallization or of constitution, in both these cases the water is called, water of hydration, as an hydrate is a substance formed by the combination of water molecules with a substance e.g.

(1) Chlorine hydrate $\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$.

(2) Calcium hydrate $\text{Ca}(\text{OH})_2 : a. \text{CaO} \cdot \text{H}_2\text{O}$.

(3) Hydrated copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Decrepitation. Some crystals during their formation : e. substances crystallizing from water, may retain varying amounts of water simply enclosed mechanically in the crystals. When such crystals are heated, the water is changed into steam and the crystal is thereby torn apart often with a crackling sound. This behaviour of the crystals is called 'Decrepitation' e.g. NaCl .

As there are only few systems of crystals and a large number of substances that crystallize, we come across different substances assuming the same crystalline form. Similarly some substances solidify or acquire according to circumstances different kinds of crystalline forms. Thus substances may be :—

(1) Dimorphous (di=two, morphe=form).

(2) Polymorphous (polys=many; morphe=form)

(3) Isomorphous (iso=like; morphe=form).

(1) When one substance has two crystalline forms it is said to be dimorphous e.g. carbon (diamond and graphite). Sulphur (monoclinic and rhombic) and this behaviour is known as dimorphous (Dimorphism).

(2) When one substance has more than two crystalline forms then it is said to be polymorphous e.g. phosphorus (white, scarlet, black). Arsenic (yellow, black

and grey). And this behaviour is known as polymorphous (Polymorphism).

(3) When different substances assume the same crystalline form i.e. they belong to the same system of crystals they are said to be isomorphous *e.g.* zinc and nickel sulphates. And this behaviour is called isomorphous (Isomorphism)

N.B. Note the distinction between polymerism and polymorphism and also between isomerism and isomorphism.

CHAPTER XI

Solutions.

During the discussion on the nature of substances we have already seen that there is a class of bodies which cannot be definitely put down either as compounds or, as mixtures. This class we styled as solutions (se = apart, and luo = to loosen) and defined it as follows :—

A solution is a body of homogeneous character, the composition of which can be continuously varied within certain limits

Solutions can be of nine types in all, as we have three states of matter – solid, liquid and gaseous –.

I. Solutions of gases in gases

When two gases are brought together they mix up quite freely and such a mixture of gases we rarely think as a solution, but it conforms with all the conditions of solutions. Here the properties are of a very simple character

All gases mix freely in all proportions provided they have no chemical effect on each other, and if the volumes and pressures are equal before they are mixed with each other, then they will have double the volume (sum of the two volumes) for the mixture if the pressure on the mixture is to be the same as before i. e. if the pressure is constant. Now from the – ‘Law of Partial Pressure’ it can be very easily seen that of this whole pressure, one half will be due to each of it, if it alone existed in the new double volume. Hence when dealing with a solution of gases we may assign to each its fraction of the total pressure, which will be the same as if the other gases were removed. This fraction of the pressure as we already know is to be called the ‘partial pressure of the gas.’

Since there is no expansion or contraction when gases are mixed, the density of a mixture can be calculated from the densities and percentages of the constituent gases.

II. Solutions of gases in liquids

The gases as a class are soluble in liquids and they fall into two heads.—

- (a) Highly soluble gases.
- (b) Very little soluble gases

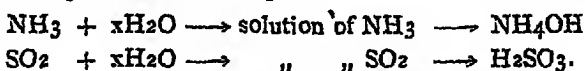
The solubility is generally expressed in terms of one— or hundred— volumes of the solvent to the volumes of the solute : c here the gas

The solubility of different gases is different as said above, and depends upon the following four factors :—

- (1) Specific properties of the gases.
- (2) Specific properties of the solvent.
- (3) Pressure put upon the system — gas and the solvent.
- (4) Temperature. Here the solubility should be inversely proportional to the temperature as per Charles's law, but it is not exactly proportional. It has to be determined.

If the gases are very soluble then they do not obey Henry's law, because the specific properties play an important part, as these make the gases go out of the pail of being the solute and form compounds of different types. There is always a change in the volume and the density also, and solutions of this kind as a rule acquire quite different properties from those that of the either constituents, in addition to the existing ones. This behaviour can be explained by assuming that the gases form chemical combinations with the solvent. Thus : the gases ammonia NH_3 or sulphur dioxide SO_2 when passed into water first form the solutions of ammonia or sulphur dioxide and

then the gases while in solution form the compounds ammonium hydroxide NH_4OH , and sulphurous acid H_2SO_3 . When these gas molecules are taken away from their solution condition to form the compounds naturally there is more room for the gas and thus more goes in solution than is required by the law of Henry.



Solubility of mixed gases

When a mixture of several gases is maintained over a liquid each of the gases of the mixture dissolves quite independently of the pressure of the other and the solubility of the dissolving gas is in accordance with its own partial pressure (cf. Dalton's Law of Partial Pressure). As for example when air is enclosed over water at 760 mm. then $\frac{1}{5}$ of this pressure, namely 152 mm., is due to oxygen, and $\frac{4}{5}$ or 608 mm. is due to nitrogen. According to the Law of Partial Pressure the quantity of oxygen dissolving in water exposed to air will be the same as if water were confined in a space containing only oxygen at a pressure of 152 mm. Similarly when a solution of a gas other than nitrogen or oxygen is exposed to the open air the gas will in general escape, for there is no opposing partial pressure to keep it in solution (cf. corollary of Henry's law).

From the above it follows that if one gas is bubbled through a solution of the other, then the originally dissolved gas must disappear and hence when a solution is boiled we get rid of the dissolved gas.

Constant boiling solutions: If the vapour pressure of a highly soluble gas and the vapour pressure of water with their ratios by weight of the gas to the steam, in the atmosphere over the solution, come to be the same, as the ratio of the dissolved gas to the water in solution, then the partial pressure will be steadily maintained and therefore the solution will boil without any change in the concentration. e. g. Hydrochloric acid gas and water.

III. Solutions of liquids in liquids.

Gases we have seen are freely miscible into one another. The liquids are fluids like the gases, and we expect that on account of the mobile nature of that state the different liquids also should freely mix. But it has on the contrary been found that some liquids do not mix at all, while others do so to a little extent only. Thus we have liquids which are :—

- (a) freely miscible i. e. completely soluble, e. g. glycerine and water, or alcohol and water.
- (b) partially soluble. e. g. ether and water.
- (c) not soluble at all. e. g. chloroform and water, oil and water etc.

When the solutions of these liquids are tested, then it is found that :—

- (i) qualities are retained in solution e. g. alcohol and water.
- (ii) qualities (new) are acquired along with the old ones. e. g. acids and water.

Properties of liquid solutions:

(1) Vapour Pressure: Each liquid before mixing has its own vapour pressure at the particular temperature. But after mixing each liquid gets its vapour pressure diminished by the other so that the vapour pressure of the solution is never equal to the sum total of the two liquids. It is greater or less than either of the vapour pressures of the liquids taken separately or it may have an intermediate value. It also depends upon the relative concentration of the liquids.

In any case the vapour from the solution will be a mixture of that of each liquid, provided that each liquid has a sensible vapour pressure.

(2) Boiling Point. On heating a mixture of liquids the total vapour pressure increases and the boiling point is reached when the pressure of the combined vapours equals the atmospheric pressure. We can have no idea as to the boiling

point of the solution from the boiling points of the liquids. It may be higher or lower than that of the either constituents. Usually it is of an intermediate value. The composition of the liquids will vary during boiling according to the amount of the vapour pressure decreased and hence the boiling point will not be a steady one but will remain moving on steadily. A solution therefore as a rule has no constant boiling point.

(3) **Fractional Distillation** As we have seen above, that liquids (solutions of liquids) have no constant boiling points, the amount of the vapour given out will depend upon the amount of the vapour pressure of the liquid (particular) and thus one liquid may leave the boiling solution more in quantity than its companion, and thus it may be possible to get the two mixed liquids separated. This process is called **fractional distillation**, as the liquids are collected in small portions by distilling the mixture.

(4) **Constant Boiling Solutions** It occasionally happens that there is one particular concentration of a solution, which has a lower vapour pressure (higher boiling point) than any other concentration or than that of the either constituent taken separately. When such a solution is distilled, one or the other constituent vapourizes first, the concentration tending towards that of the lowest vapour pressure. When this concentration is reached, the solution boils with a steady *i.e.* constant boiling point as if it were a pure substance, and the distillate has the composition as the solution remaining in the still. Such a constant boiling solution cannot be altered in its concentration *i.e.* proportions of the constituent liquids, by repeated distillations *e.g.* nitric acid and water.

IV. Solutions of solids in liquids

We have already seen that we come across two types of solutions: (1) Simple or true. (2) Chemical or apparent. When a solution of a solid dissolved in a liquid, leaves the

solute in its original chemical condition then it is a true solution ; but when zinc (metallic) is dissolved by sulphuric acid, then it is not a true solution as we do not get back zinc in its original metallic condition.

Solubility of solids in liquids is governed by the same conditions as the solubility of gases in liquids, *i. e.* on the —

- (1) Specific properties of the solids.
- (2) Specific properties of the solvents.
- (3) Pressure.
- (4) Temperature. Here it varies as the temperature and is usually higher and higher as the temperature rises, except in the case of the calcium salts.

Saturated solution . When a quantity of a solvent cannot any more dissolve the solute at that temperature then such a solution is called a saturated solution.

Supersaturated solution : Often times when during the cooling of a solution the solute —solid— is kept away and not allowed to be in it, then often the excess of the solute fails to crystallize out of the solution. The solution will contain then more quantity of the solid —solute— than is necessary for the saturation concentration, and this is called then a 'supersaturated' solution. Such a solution which is having lower temperature than the normal one for that concentration, is also called the supercooled solution. This case occurs in the case of very soluble solids containing much water of crystallization *e. g.* sodium sulphate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; sodium thiosulphate (hypo) $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Potassium alum $\text{K}_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$ or in general where the solution becomes syrupy.

At the least disturbance, either by shaking or by throwing a crystal of the solute, the excess crystallizes out, as the saturation is the equilibrium state.

Effect of temperature on the solubility. As already mentioned the solubility in general increases with the rise of temperature. In a few cases like calcium salts the solubility decreases at the rise of temperature

Regularities observed in solutions

A study of the physical qualities of a solution has brought to light certain regularities in the behaviour of the solutions provided they are (1) dilute and (2) are not of electrolytes. These are —

(1) Lowering of the vapour pressure.

It is found that the vapour pressure is lower than that of the solvent, and this lowering has been found out to be depending upon the molecular weights of the solute, and equivalent or equimolecular weights have the same effect.

As a corollary of the above state of vapour pressure we notice the change in the freezing point and the boiling point of the solution. Thus :—

(2) Lowering of the freezing point of the solutions

It was noticed that a salt solution does not freeze exactly at 0°C but the point is lower than 0°C . It is now well-known that equimolecular weights (in dilute solutions) lower the freezing point of the solution to the same limits.

(3) Elevation of the boiling point of the solution.

As the vapour pressure is lowered naturally the boiling point has to rise to allow sufficient quantity of the vapour to be gathered so as to overcome the pressure from above (the liquid). This is only possible if more heat is applied.

(4) The osmotic pressure changes

Osmotic Pressure

It is but natural that, if two substances come in contact with one another then there is bound to be mutual influence exerted. If these two substances coming together are solids

then we are not always able to notice the pressure exerted, for the simple fact that on account of the strong opposite unyielding pressure the two are apparently without any effect. But that is not really so can be easily seen if we take a heavy body and place it on one which is brittle. What we find in such a case is that the brittle body gives way and allows the other body to occupy space inside its own volume and thereby increasing in volume. Similar phenomena occur in other states. liquids and gases, especially solids pushing in liquids. In the case of gases they mix freely with each other and we are not able to notice the individual force except in the diffusion experiments. While in the case of liquids or rather solutions of solids, we notice that if two substances are kept in contact then they will try to mix with one another. But if these are kept separated by a partition which acts like a filter paper and allows one kind of the material to pass through, then as one can pass into the other while the reverse is not possible, the quantity in one increases and naturally the volume gets increased while in the other contrary is the case. Now where the quantity increases i. e. the number of particles increases, it brings about naturally extra pressure exerted. This pressure is called the osmotic pressure.

A solute when it dissolves, it distributes itself through the solvent, i. e. it tries to diffuse in the whole mass of the solvent and while doing so it exerts a certain pressure on the solvent in pushing itself through it. This push pressure (osmos = impulse, or push) is called the "Osmotic Pressure", and can be indicated by the push or the force which it imparts on the (parchment) arrangement for registering the force. We as a rule rarely notice the existence of any such force or gain any idea of its magnitude, because it is only when diffusion can be prevented that the force becomes apparent.

Osmotic Pressure Demonstration.

A funnel with a long stem is closed on the broad side by a parchment paper quite tight. The vessel so prepared is filled

with a concentrated solution of sugar upto the neck of the stem. The vessel is then placed in a dish as shown (fig. 14). The sugar cannot pass through the parchment and distribute throughout the water in the dish but the water can pass and passes into the bell. But this brings about an increase in the volume of the solution in the bell and thus the level of the solution in the stem of the bell rises until the force of the osmotic pressure is balanced by the hydrostatic pressure of the column of the liquid.

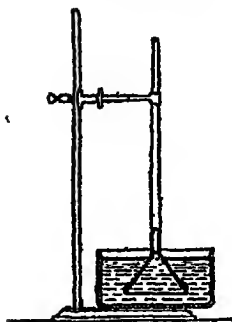


Fig. 14.

History Dutrochet in 1726 filled a glass vessel with copper sulphate solution and closed its opening with a tight bladder. When immersed in water the contents of the vessel increased so, that the bladder was extended and eventually it burst.

Abbe Nollet in 1750 made a similar experiment using alcohol instead of copper sulphate solution.

Priestley in 1854 noticed that the protoplasmic contents of certain vegetable cells contracted when placed in a concentrated salt solution. With a weaker solution of the salt the contraction is less, and in pure water the cell maintains its form. This happens so, since expansion is promoted by the rigid outer cell-wall which is pervious to both and the substance in solution. The protoplasmic contents are enclosed in a membrane which has the property of allowing pure water to pass but which is impervious to most dissolved substances.*

By carefully diluting a concentrated solution of a salt and making trials for similar cells, a concentration is eventually obtained which just causes no change of form in the cell contents. A number of solutions of different salts may be adjusted in strength so that each is in equilibrium with similar cells. These solutions are then said to have equal osmotic pressure or to be 'isotonic'.

* A very instructive experiment can be performed with ordinary eggs and a dilute solution of hydrochloric acid and a concentrated solution of calcium chloride.

This statement assumes that two solutions isotonic with a third one are isotonic with one another. Quantitative experiments of this nature were made by de Vries in 1884-88. He showed for example, that solutions of potassium nitrate, potassium chloride and sodium nitrate are isotonic, in the above sense with one another where they had chemically equivalent -or molecular- concentrations

The nature or the cause of Osmotic Pressure

The nature or the cause of osmotic pressure has formed a subject of considerable discussions and final agreement has not been yet arrived at. The following are the causes that effect osmosis.

I. **Chemical** The osmotic pressure is due to the attraction between the solute and the solvent. These tending, for instance to form hydrates

II. **Physical.** The tendency of a gas to expand so as to fill any vessel containing it, may be compared with the expansion tendency of a solute to fill the liquid space at its disposal

(a) Osmotic pressure is due to the bombardment of the solute molecules. The solvent molecules can pass the diaphragm freely and so produce no pressure on it

(b) The diaphragm is subjected on the outside to the bombardment of the pure solvent molecules only and on the inside to that of both the solvent and the solute

(c) Two vessels of equal volumes are separated by a wall of palladium (metal). One is filled with hydrogen and the other with nitrogen at the same pressure P . The apparatus is heated to 600°C . Hydrogen passes. On cooling to the original temperature, there will be a pressure of $\frac{1}{2} P$ in one vessel and $1\frac{1}{2} P$ in the other. The excess may be regarded as the osmotic pressure

(d) Combination of the solvent with the solute molecules diminishes the mobility. The mobility of the pure solvent molecules being greater there will be a flow from outside to inside, and the pressure within the cell will increase, but the mobility of the liquid molecules becomes greater as the pressure increases so that when the pressure reaches a certain value, the mobility of the molecules inside will become equal to that of the pure solvent molecules and the flow will then cease

(e) In pure water there is an equilibrium between the associated $-(H_2O)_n-$ and the simple $-H_2O-$ molecules, and the effect of introducing the molecules of the solvent—non-electrolyte—is to cause dissociation of the complex water molecules to an extent which is in proportion to the amount added. The osmotic pressure is a measure of the extent to which the equilibrium is disturbed in the direction —



Difficulties in determining the Osmotic Pressure.

Considerable difficulties are encountered in determining the osmotic pressure. These are —

- (a) The maximum pressure is only reached after a very long time
- (b) The pressure produced may be very great and so cause bursting or breaking of the apparatus. A 17% solution of ammonia could give at 0°C a pressure of about 224 atmospheres
- (c) No perfect semi-permiable membrane has yet been obtained one which is completely impervious to the solute but is pervious to water

Laws of Osmotic Pressure

The laws of osmotic pressure are very nearly similar to the laws that are obeyed by the gases. The only thing that is here to be imagined is that the intervening spaces between the different gas molecules are filled in by the solvent. Thus :—

- (1) The osmotic pressure is proportional to the molecular concentration of the solution and does not depend upon the character of the solute (provided it is not an electrolyte)
- (2) The osmotic pressure is proportional to the absolute temperature so that, it exerted by a substance in solution, is equal to the gas pressure which it would exert if it were a gas occupying the same volume as that of the solvent

N.B. Osmotic pressure plays an important part in the physiological processes of plants as many animal and vegetable membranes are semi-permiable and allow one thing to pass through them and withhold the other

Conclusion: From the foregoing descriptions and explanations, it is quite evident that the three physical constants -freezing point, boiling point and osmotic pressure- are affected to an equal degree by the same molecular quantities of the dissolved substances. It is the relative number of the molecules and not the quality of the molecules that is the governing or the deciding factor in these changes.

The picture which is presented to us by these changes of the physical constants is quite similar to the one of the kinetic theory of gases. The different kinds of molecules here appear themselves to distribute throughout the whole body of the solvent much as a gas distributes itself in the space in which it is enclosed. The osmotic pressure that these produce, is quite analogous to the pressure of a gas, and similarly other effects are also dependent merely upon the number of molecules that are present in a given volume of the solvent, exactly in the same fashion as the effects produced by a gas are dependent upon the number of molecules confined in a given space.

CHAPTER. XII.

Acids, bases and salts.

There were and there also are, different systems of classification of compounds. In former times the chief points for differentiation were the apparent properties of the different compounds, and thus sometimes substances which have been found now of very widely different constitution had been classed into the same groups. Following the same crude method of classification, old chemists classed together all substances tasting sour, like vinegar, and gave them the common name 'acid' (from acetum = vinegar, acidus = sour from ac = point). The other substances tasting like wood-ashes which are of opposite nature to that of the acids, they styled them as 'bases' meaning that these are as if the fundamental principles i.e. starting substances for the formation of the salts. The compound which is got by the double decomposition of caustic soda and hydrochloric acid is the substance salt -common salt-. Hence any substance formed in the similar fashion is called a 'salt'. (Salt indicates the method of formation).

Putting down the formulæ for different acids and bases :—

	Acids.	Bases
a	{ HCl	KOH
	{ HBr	NaOH
	{ HI	Ca(OH) ₂
	{ H ₂ S	Ba(OH) ₂
b	{ HNO ₃	Al(OH) ₃
	{ H ₂ SO ₄	Sn(OH) ₄
	{ H ₃ PO ₄

we see that these compounds have some elements common in all of them, or better we find that all acids have 'hydrogen' common—no matter the varying number—and all bases have 'hydrogen + oxygen' common. This hydrogen and oxygen together is called 'Hydroxyl' from Hydro-gen-oxy-gen-yl where 'yl' is used to denote the adjectival force.

Thus from the general information we can define an acid or a base as:—

An acid is a compound which contains hydrogen, is sour to taste, is corrosive in action on the skin, and changes blue litmus to red and keeps red litmus red.

A base is a compound which contains the 'hydroxyl' combination, is soapy to touch, ashy to taste and is also corrosive but changes red litmus to blue and keeps blue litmus blue

N. B. With regard to the substances that change their colour the decisive point is the colour (change) that persists at the end. And the best way to remember the present colour is from the initial letters of the words 'base' and 'blue'. Thus:—

Acid \longrightarrow Red
Base \longrightarrow Blue.

Most of the acids are produced from the oxides of the non-metals and water. While bases are produced in a similar fashion with oxides of the metals and water.

The reaction of a solution of a base is also called 'alkaline' reaction, because the common bases caustic soda NaOH and caustic potash KOH are called 'alkalies', because the alkalies were obtained by calcining various materials and reducing them to ashes (kohol = ash, impalpable powder); and thus a reaction which is produced by solutions of the alkalies gets the name 'alkaline' in preference to 'basic' and thus basic or alkaline stand as synonyms.

Classification and nomenclature of acids and bases.

Looking at the different formulæ of the acids (on page 126) we see that though all the acids have hydrogen in common,

still there is one marked difference between the different formulæ and it is this that some have oxygen in the formula (molecule) whilst others have not any oxygen in the molecular formula. From this presence or absence of oxygen in the molecule they are styled either as *oxy-acids* or *hydro-acids*.

$\begin{array}{l} \text{Acids} \begin{cases} \text{oxy-acids} & \text{HNO}_3 \text{ etc.} \\ \text{hydro-acids} & \text{HCl etc.} \end{cases} \end{array}$

Thus :

(i) *Oxy-acids* are those which contain both oxygen and hydrogen as well, e. g. HNO_3 , H_2SO_4 , H_3PO_4 etc.

(ii) *Hydro-acids* are those which contain only hydrogen or in which oxygen is absent, e. g. HCl , H_2S etc

The naming of the hydro-acids is done by using the prefix 'Hydro' and a suffix 'ic', and inserting the name of the element from which the acid is formed in the middle. Thus —

(i) $\text{HCl} \longrightarrow \text{Hydro-chlor-ic} \longrightarrow \text{Hydrochloric.}$

(ii) $\text{H}_2\text{S} \longrightarrow \text{Hydro-sulphur-ic} \longrightarrow \text{Hydrosulphuric}$

As for naming the 'Oxy-acids' the prefix hydro -indicative of only hydrogen- is dropped, and only the suffix 'ic' is used with the name suggestive of the element. Thus .

$\text{HNO}_3 \longrightarrow \text{Nitric - ic} \longrightarrow \text{Nitric.}$

$\text{H}_2\text{SO}_4 \longrightarrow \text{Sulphur - ic} \longrightarrow \text{Sulphuric.}$

$\text{HClO}_3 \longrightarrow \text{Chlor - ic} \longrightarrow \text{Chloric.}$

The acid formula which has less oxygen than in the usually occurring compound -acid- gets the suffix 'ous' instead of 'ic'. Thus :

$\text{HNO}_2 \longrightarrow \text{Nitric - ous} \longrightarrow \text{Nitrous acid}$

$\text{H}_2\text{SO}_3 \longrightarrow \text{Sulphur - ous} \longrightarrow \text{Sulphurous acid}$

$\text{HClO}_2 \longrightarrow \text{Chlor - ous} \longrightarrow \text{Chlorous acid.}$

For other powers of oxygen either 'per' or 'hypo' are used, as prefixes according to the oxygen contents which are more than 'ic' or less than 'ous.' Thus .—

$\text{HClO} \longrightarrow \text{Hypo-chlor - ous} \longrightarrow \text{Hypochlorous acid}$

$\text{HClO}_4 \longrightarrow \text{Per - chlor - ic} \longrightarrow \text{Perchloric acid}$

The bases are generally called 'hydroxides' as herein hydrogen and oxygen act together as if they are one entity. The naming is done by using the name of the metal as a prefix to the word hydroxide. Thus :—

KOH \longrightarrow Potassium hydroxide.

$\text{Cu}(\text{OH})_2$ \longrightarrow Copper hydroxide.

But when the metal has two hydroxides then the name of the one with the smaller number of the hydroxyl groups ends in 'ous' while the other ends in 'ic'. Thus :

$\text{Cu}(\text{OH})$ \longrightarrow Cuprous hydroxide and

$\text{Cu}(\text{OH})_2$ \longrightarrow Cupric hydroxide.

$\text{Hg}(\text{OH})$ \longrightarrow Mercurous hydroxide and

$\text{Hg}(\text{OH})_2$ \longrightarrow Mercuric hydroxide.

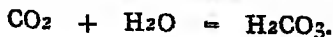
The hydroxides in general, as we can gather from the foregoing information are 'bases', and have their (those that are soluble) reactions towards litmus which may be either said as 'basic' or 'alkaline'.

A.—Preparation of Acids:

Acids, as can be gathered from the meaning of the word oxygen, are compounds that are got by passing certain oxides—non-metallic—in water. But acids also result from the reactions other than the above one. Thus acids can be prepared by .—

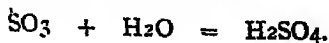
I. Bringing the (non-metallic) oxides and water together

- (a) Carbonic acid gas when passed into water results in the formation of carbonic acid.



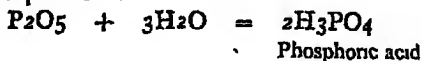
Carbonic acid.

- (b) Sulphur trioxide a liquid passed into water gives sulphuric acid



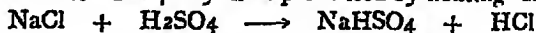
Sulphuric acid

- (c) Phosphorus pentoxide a solid thrown into water gives the phosphoric acid.

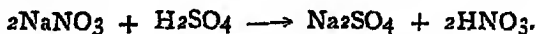


II. Liberation of it from its salt Whenever possible the salt is treated with sulphuric acid, care being taken that the reaction be not stopped and the acid be easily liberated.

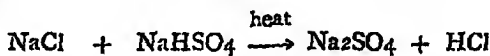
- (a) Formation of a pasty mass prevented by heating HCl



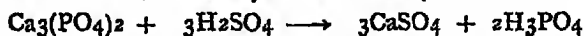
- (b) The liberation of the acid may be helped by heat HNO_3 .



or better



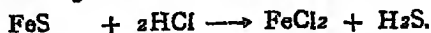
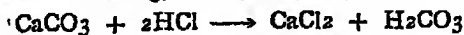
- (c) Instead of heating, water may be added H_2CO_3 , H_2S , H_3PO_4 .



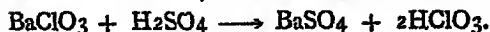
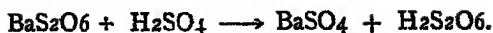
- (d) Whenever the acid required is a reducing agent, sulphuric acid ought to be replaced by phosphoric acid HBr , HI .



- (e) Hydrochloric acid may replace sulphuric acid in many cases H_2CO_3 , H_2S , H_3BO_3 .

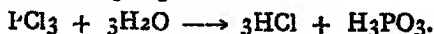


- (f) The salts of barium with sulphuric acid yield at ordinary temperature the total amount of the acid contained. $\text{H}_2\text{S}_2\text{O}_6$, HClO_3



- (g) Similarly with salts of lead and hydrogen sulphide :
 $\text{H}_4\text{P}_2\text{O}_7.$
- (h) or a silver salt with hydrochloric acid . $\text{H}_2\text{N}_2\text{O}_2.$
-

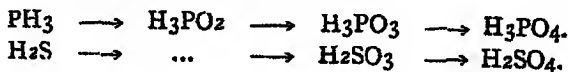
III The decomposition of the non-metallic chlorides : $\text{H}_3\text{PO}_3.$



IV. The oxidation :

- (a) of non-metals in presence of water : HNO_2 , H_3PO_3 ,
 $\text{H}_2\text{SO}_4.$
- (b) of peroxides of certain metals: Heating a lower oxide with a mixture of potassium nitrate KNO_3 and potassium carbonate Na_2CO_3 or both :
 HMnO_4 , $\text{H}_2\text{CrO}_4.$

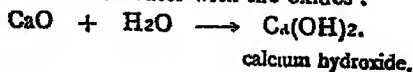
N.B. The acidity seems to increase with the amount of oxygen present in the molecule.



B.—Preparation of bases :

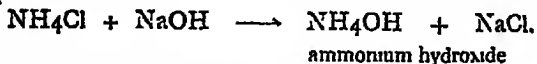
Bases which are otherwise styled hydroxides are formed in the case of metals of the alkalis (Na , K and NH_4) and the alkaline earths (Ca , Ba , Sr and Mg) by :—

- (1) Direct union of water with the oxides :



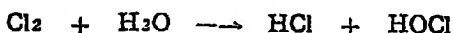
and in other cases by —

- (2) Double decomposition when a soluble hydroxide acts upon a salt :



Neutralization or salt formation .

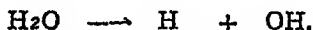
When chlorine gas is passed into water we find that it gives us two substances hydrochloric acid HCl and hypochlorous acid HOCl .



From the formation of hypochlorous acid and hydrochloric acid it is evident that the water molecule got split up not in the form as —



but as .—

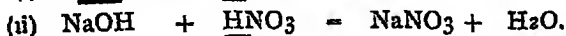


Thus it is clear that if H and OH come together under favourable conditions, these will combine and form water, leaving the other components of both the compounds, containing H and OH , free. These components now are free to and have to combine with one another. This combination is called a 'salt' from the very common substance the common salt which is also obtainable from a similar reaction

Caustic soda + muriatic acid = water + common salt.



In the similar fashion we get —



Thus potassium chloride KCl , sodium nitrate NaNO_3 , and calcium sulphate CaSO_4 are called salts, and the whole reaction with the ultimate result of the formation of salt is called 'salt formation.'

If the reacting substances are tested with litmus paper before these are mixed together, we notice that each has its own colour change and this colour change is of opposite character. When adequate quantities of these substances are brought together there is no effect seen on the litmus paper, and this absence of the effect is attributed to the qualities of the reacting substances being nullified or neutralized by their mutual interaction and hence this process also is called 'neutralization.'

We are now in a position to give a definition of a salt provided we keep in mind that the water formed during the salt formation is not a part of the salt but only an unavoidable thing during the formation of the salt, and thus it is to be excluded from the definition of a salt. Thus :—

Salts are substances formed by the interaction of acids and bases, with eventual removal of water

Having seen that the power of neutralization either of an acid or a base is solely depending upon the 'hydrogen' or the 'hydroxyl' radicals, we can easily conclude that individual acids or bases would be more or less powerful depending upon the number of the hydrogen atoms or the hydroxyl combinations in their molecules. These powers of the acids are measured with respect to bases, and of the bases with respect to acids, and thus the power of an acid is expressed in terms of the 'basicity of an acid' and the power of a base is expressed in terms of the 'acidity of a base'.

The standard for the measurements are caustic soda NaOH and hydrochloric acid HCl , which each of them has one hydroxyl or one hydrogen respectively. Thus :—

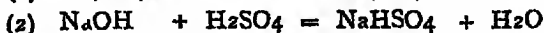
- (1) Hydrochloric acid $\longrightarrow \text{HCl}$ is a monobasic acid
 - (2) Nitric acid $\longrightarrow \text{HNO}_3$ is a monobasic acid.
 - (3) Sulphuric acid $\longrightarrow \text{H}_2\text{SO}_4$ is a dibasic acid.
 - (4) Phosphoric acid $\longrightarrow \text{H}_3\text{PO}_4$ is a tribasic acid.
- and
- (1) Sodium hydroxide $\longrightarrow \text{NaOH}$ is a mono-acidic base.
 - (2) Calcium hydroxide $\longrightarrow \text{Ca(OH)}_2$ is a di-acidic base.

Thus the capacity of the molecules of the different acids for entering into reaction with different quantities of one and the same (standard) base is called the *basicity* of the acid, and the acidity of the base is just opposite of the basicity.

When different quantities of acids and bases are brought together, it is not always the case that adequate or better, equivalent quantities are coming together, and thus from the law of Constant Proportions we will find that excess of an acid or a base is left out. But if equal quantities are mixed then we get both the acid and the base completely neutralized, and then we get what is called a *Normal salt*, from the fact that it is a normal state of things that these should be completely neutralized when we bring together equivalent quantities of the reacting substances. Thus :—



In case we get unequal quantities of the acids and bases and especially if one of them (acid or base) is of a type other than the mono, then the neutralization takes place in a semi-neutralized condition, and we get either the excess of the acid parts or the basic parts still remaining in the molecules unused. If salts are formed according to the above, then they are styled either as acid salts or basic salts according to the predominance of an acid or a base in the molecule of the salt. Thus :—



Here 'HCl' can neutralize only $\frac{\text{Ca}(\text{OH})_2}{2}$, and 'NaOH'

can neutralize only $\frac{\text{H}_2\text{SO}_4}{2}$. Thus either one 'OH' in the 'Ca(OH)₂' or one 'H' in the H₂SO₄ molecule remains unneutralized, and has thus to be shown in the writing of the formula.

Now as ' Ca.OH.Cl ' is neither a pure salt nor a pure base, but is both and this must be clearly expressed. Thus to express this it is called a 'basic-salt'. Similarly ' NaHSO_4 ' is neither a pure acid nor a pure salt but is both. And thus to express this it is called an 'acid-salt'.

In the case of these semi-neutralized salts the litmus reaction may be different than from what we expect from a mere inspection of the molecular formulæ. Many normal salts show an acidic or a basic reaction and even some acid-salts give practically a neutral reaction.

N. B. A careful distinction must be made between acid-character and acid-reaction

Both the acid and basic salts can be converted into the normal ones either by.—

- (1) Driving off the excess of the acid or the base if convenient or by,
- (2) Neutralization of the excess of the acid or the base by an adequate quantity of the base or the acid as the case may be.

Nomenclature of the salts. As a rule the salts are named with reference to the acids from which they are derived. The salts of hydro-acids have their name ending in 'ide'; as

$\text{NaCl} \longrightarrow$ Sodium chloride.

$\text{KCN} \longrightarrow$ Potassium cyanide.

However the same ending 'ide' is given to the name of the compounds of but two elements—binary compounds—irrespective of their character as

$\text{Mg}_3\text{N}_2 \longrightarrow$ Magnesium nitride.

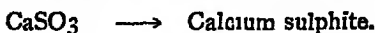
$\text{SO}_2 \longrightarrow$ Sulphur dioxide.

Salts derived from oxygen acids whose names end in 'ic' have their names ending in 'ate' as :

$\text{NaNO}_3 \longrightarrow$ Sodium nitrate.

$\text{K}_2\text{SO}_4 \longrightarrow$ Potassium sulphate.

In a similar way the prefix changes to 'ite' when we pass from a lower acid to its salts as —



C—Preparation of salts.

A great many methods are in use for the preparation of compounds called salts, as these salts are very numerous and each has its own peculiarities which must be taken into account in devising means for preparing it. In many cases some rather unusual methods are employed, owing to the character of the minerals available in nature or to the accumulation of a cheap by-product in some other industry. Naturally the methods employed on a small scale in the laboratory are likely to differ from those used in industries, where economy is the first requirement.

There are however some general principles which underlie the great majority of these methods and these are —

I. Direct union of two elements

Very many binary compounds can be prepared by heating the metal with the appropriate non-metal. Among these are sulphides and halides. The product of course is anhydrous rather than a hydrated compound. This method finds wide application when anhydrous compounds are wanted —



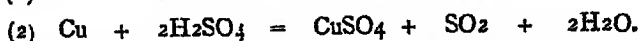
II. Direct union of the anhydrides of the acid and the base:



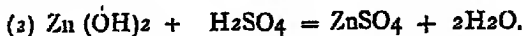
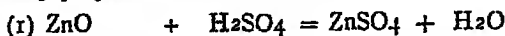
III. Treatment with an acid of a

- (1) metal, or
- (2) metallic oxide, or
- (3) metallic hydroxide.

(α) In the laboratory metals are generally used for the preparation of salts, as these are generally to be had in a degree of purity :—



(β) In the industries either the oxides or the hydroxides are usually employed, since they are as a rule found in nature or are of easy preparation



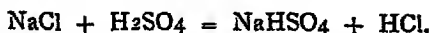
IV. Reduction of salts of oxy-acids to those of hydro-acids

Many salts of oxy-acids when they are heated with a reducing agent (carbon) get reduced and form salts of the hydro-acids



V. Double decomposition.

(α) Displacement of a volatile acid When a non-volatile acid acts on a volatile one, the latter is displaced in accordance with the general principles of equilibrium, provided the volatile acid is sparingly soluble in the liquid present



(β) Method based upon precipitation. The formation of a precipitate, when two substances such as form an insoluble product by mutual exchange of partners, are brought together in solution, takes place in accordance with the principles of a balanced reaction



VI Fusion method.

When compounds are melted together, it sometimes happens, that double decomposition occurs, which would not take place if the same salts were brought together in water. In such fusion reactions one of the melted salts may be regarded as the solvent and it is to be expected that the solubility of the other in this will be different from its solubility in water. For example barium sulphate BaSO_4 is practically insoluble in water and consequently is not greatly affected by aqueous solution of sodium carbonate Na_2CO_3 . In melted sodium carbonate on the contrary it is readily soluble, while barium carbonate BaCO_3 , is insoluble.

As a consequence when it is melted together with sodium carbonate the following double decomposition takes place.



When the mixture is cooled and then warmed with water all the compounds except barium carbonate BaCO_3 dissolve and thus may be filtered off, and converted into any desired salt

CHAPTER XIII.

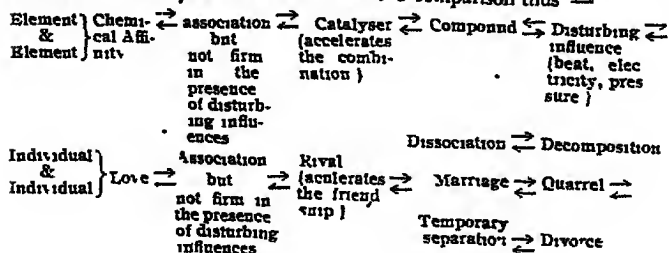
Dissociation.

We have seen that 'Chemical Affinity' and 'Kinetic Energy' are great controlling factors in the formation of compounds and eventually their stability of constitution and form. Yet on account of these very same factors, whose influence can be modified by external circumstances, we find many well formed compounds showing unstability. Some good many of these are affected permanently whilst there are yet others who alter their form and constitution to suit the surroundings and again revert to the original, when the extreneous circumstances allow.

Thus where there is a complete breaking up of the compound without any possibility of again forming the original compound we call it decomposition but where the rupture is only of a short duration till the inducing factors are powerful, then that kind of temporary breaking is called dissociation. Thus to define:

When a chemical compound splits up into simpler substances by change of physical consitions (Temperature, Pressure or Dilution) and the products of the decomposition are capable of recombining to form the original compound on resumption of the original conditions then the process of such a decomposition is called dissociation.*

* To express this idea more pointedly, we may carry further on the simile about 'affinity and love' and draw the comparison thus —

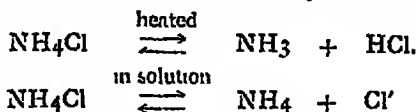


It is of two kinds —

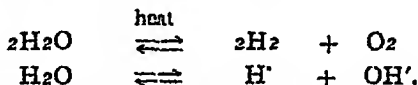
- A. (1) Dissociation (when heated) Thermal
 B. (2) „ (in solution) Electrolytic

A — Thermal Dissociation

Here it must be well remembered that the components of the two kinds of dissociation—Thermal & Electrolytic— are not necessarily the same, nay they are usually different Thus



Whilst .



Thus we see that the points of attack for different factors are different and we get altogether different radicals

It is evident that the term dissociation applies to only reversible reactions as it is here that a compound may break and again form over and over again, depending upon existing conditions. Thus —

When KClO_3 is heated the products formed by heating cannot be recombining again to KClO_3 because this is a non-reversible reaction and hence classed under decomposition.

Similarly also when sugar is heated, the products of the decomposition that takes place cannot be made to recombine so as to form the original sugar. The sugar which has been transformed, which, like the chlorate of potash, is changed once and for all The decomposed molecules remain decomposed Here there is no question of Kinetic Equilibrium, the action is not a balanced one

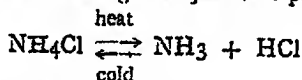
While $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ is a reversible reaction, and hence can be classed under dissociation

Proof:—When a solid or a liquid is heated to a sufficiently high temperature it changes to a gas, and this gas has a

certain volume according to the temperature and this volume eventually imparts a certain pressure. From the Kinetic Theory of gases the pressure depends upon the number of particles in the volume : *i. e.*, the pressure depends upon the density. So the pressure would be a direct reading of the density.

Now in certain cases it has been found out that the density gets lower or higher as the temperature is increased or decreased. If then there is a change in the density it clearly shows that there must be a change in the number of the particles contained in the volume : *i. e.*, the number either increases or decreases as the conditions change.

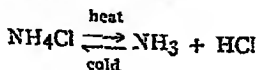
Therefore as the number is changed and as no other substance is added the natural conclusion that can be drawn from this is that the original molecules of the gas must be either associating or combining with one another, or dissociating *i. e.*, splitting into smaller ones. Deville was foremost in investigating this question. He soon proved that decomposition always takes place in such cases and substantiated his statement by taking the example of ammonium chloride wherein the following changes were proved to occur.

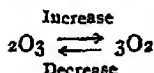


Here it is plain that every molecule of ammonium chloride which thus dissociates yields a molecule of ammonia and one of hydrochloric acid gas, making in all two molecules in place of one. Hence the mixture of two gases must exert double the pressure if the volume is constant or must occupy twice the space and thus consequently must possess but half the density.

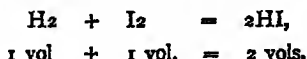
When the number changes then the pressure on the sides must change as the sides of the containing vessel are differently affected.

The following are some of the most common and hence important cases of dissociation by heat.





III — From this rule it follows that if the volume does not change on displacement of equilibrium at constant temperature alteration of pressure should have no effect on the position of the equilibrium —



The whole matter about thermal dissociation is placed beyond doubt by experimental proofs from the cases like that of ammonium chloride which when special precautions are taken can be vaporized without decomposition, and not only this but when thus vaporized is found to possess a density in good agreement with the anticipated value.

Thus the facts that both decompositions as well as dissociations take place are proved beyond doubt and still "The proof that in this instance Avogadro's hypothesis is not wrong affords naturally a far stronger confirmation than a score of normal straight forward cases."

B.—Electrolytic Dissociation.

Solutions and particularly those aqueous solutions of salts, acids and bases, form one of the most important classes of chemical substances, and to the above categories almost all inorganic, and some organic compounds belong.

In solution the behaviour of acids, bases and salts has been found to be quite abnormal especially with regard to the physical constants: boiling points, freezing points and osmotic pressures. This abnormal behaviour is so marked a one that compounds in general have been divided on the one hand into indifferent substances and these are mostly organic; and on the other acids, bases and salts. In addition to the unusually abnormal effects given by the latter substances in solution, there is yet another distinction marking them off still more sharply.

Solutions of these compounds act as conductors of electricity while those of the indifferent substances lack in this property

One thing however here to be particularly borne in mind is this that it is the solutions of the acids, bases and salts that have this power and not the pure substances themselves. Thus for example liquid hydrogen chloride i. e. liquefied hydrochloric acid gas or pure hydrogen sulphate i. e. absolute sulphuric acid which has been very carefully prepared and freed from the last traces of impurities does not conduct electricity to any measurable extent. These purified acids do not attack metals or affect litmus, is quite a highly significant fact. Similarly water which has been prepared absolutely pure by redistillation from platinum apparatus and also freed from the smallest quantities of dissolved gases— a most difficult task— can hardly be said to show the least conductivity

In spite of the non-conductivity of either the pure acid or pure water, yet if these are mixed together, the solution allows electricity to pass with as much ease as a metallic wire like that of copper. Similarly the solution now attacks metals, and changes blue litmus to red etc just as the ordinary impure acids of commerce would do

Thus we find that the solutions of acids, bases and salts do not behave in the usual way. It has already been observed under the chapter on solution that

(I) The Boiling Point, the Freezing Point and the Osmotic Pressure of a solution depend upon the number of particles (molecules) dissolved in the solution.

(II) The Boiling Point or Freezing Point or Osmotic Pressure depends upon the number (of molecules) and not upon the quantity (of the substance), the more the number the more pronounced are these states

(III) Then again these regularities are only observed in the case of solutions of substances other than acids, bases or salts (to be called electrolytes).

Now let us consider the conditions of solutions of these (of salts, acids and bases).

These solutions show certain other qualities acquired in addition to the former ones :—

- (1) Freezing point is lowered
- (2) Boiling point is raised.
- (3) Osmotic pressure is increased.

The deviation from the calculated effects varies within wide limits. In some :—(A) It is slight

In some :—(B) It reaches double or triple value depending upon the "concentration" and is utmost in very dilute solutions.

Now in the former cases (to be called non-electrolytes) it is found that the boiling point etc., depend directly upon the "number of molecules" dissolved, and not on their individual characters or qualities. Can we not suppose these deviations as due to the change in the number of independent particles? Such an explanation we have adopted in the case of gases and we have found it out to be true and hence that very same explanation is resorted to and adopted here

So it is assumed that the solute dissociates, i. e. splits up into small particles, behaving themselves as independent bodies or entities.

Historical development of the idea of electrolytic dissociation

It will be quite interesting at this point to give a short historical outline of the main theories of electrolysis which have been advanced from time to time.

In 1780 Galvani noticed that the action of an electric current on the frog and Volta extended the knowledge about electricity a good deal. And it was he who suggested that friction of two dissimilar bodies was sufficient to make them endowed with electricity of opposite nature (polarity) In 1807 Davy advanced this view further by holding that the smallest particles of substances (atoms) become positively electrified upon contact (the intensity of the charge rising with increase of temperature)

and also that chemical combinations result from the neutralization of the opposing potentials. The signs of the potential of the combining elements could be experimentally determined. Electro-positive elements are isolated at the negative poles and vice versa, upon electrolysis.

In 1812, and more fully in 1819 Berzelius published the **Dualistic Theory** of chemical combinations. This has a great resemblance to Davy's in some fundamental points, but differs in that it was more systematically developed. He maintained that every atom possesses both + ve and - ve electricity but in varying amounts. Thus some elements were positive and others negative. Most elements were positive with respect to some and negative with regard to the others. Only oxygen was never positive to any element, and thus was held to be purely electro-negative and for this and other reasons as well Berzelius adopted it as his standard. The elements after combination furnished new bodies which again had an excess of one or the other kind of electricity present. Thus the basic oxides resulted from the union of oxygen and strongly electro-positive elements (the metals) and similarly acid oxides are the result of combinations between oxygen and non-metallic elements. Salts and even mixed salts and hydrated salts were regarded as the product of union of the already compound bases and acids. Here also an excess of one or the other kind of electricity is being left over, but that in a less pronounced quantity than with similar substances.

However in 1839 Daniell demonstrated and proved that during electrolysis the same amount of electricity will set free quite a definite amount of hydrogen on being passed successively through water and a solution of sodium sulphate. Yet in the latter case (Na_2SO_4) it will liberate also an equivalent amount of sodium hydroxide. Thus doing double as much work in the second as in the first instance according to Berzelius's theory. Moreover the dualistic hypothesis did not precisely explain the peculiar behaviour of certain acids as compared with others. Thus it could not say why certain hydro-acids (notably HCl) were as strong or stronger, than many oxygen acids containing the most electro-negative elements of all. Thus there were many objections to this dualistic theory and a theory which was accepted and found its way into text-books for many years was that of Grotthus (1805).

According to the theory of Grotthus the molecules of an electrolyte, though previously indiscriminately distributed through the solution, arranged themselves in "chains" through the liquid under the influence of

the electric current and the particles adjacent to the electrodes then separating as in fig 15

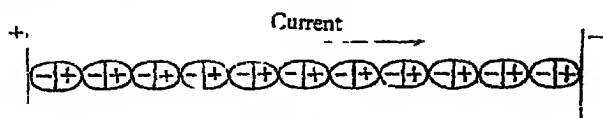


Fig 15.

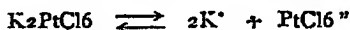
Clausius in 1854 applied the kinetic theory to electrolysis. He assumed that the electrolyte molecules were in constant motion in the solution and hence they are momentarily split up into their ions. Under usual conditions recombination took place at once, but in presence of an electric current the ions were separated at the electrodes, a mutual interchange of component parts ensuing between the electrodes. Both the above theories were not accepted as each presupposes a certain minimum electric current to be necessary for electrolysis, whereas the smallest current will effect electrolytic decomposition.

The next in the field was Arrhenius who in 1887 advanced his 'Ionic Theory' of electrolysis which was already foreshadowed as early as 1833 by Faraday. Arrhenius assumed that all electrolytes (according as they are good or bad conductors) are more or less dissociated in solution into positive and negative ions carrying charges of 'positive' or 'negative' electricity in proportion to their valency. The electric current simply acts as a directing force and causes the ions to migrate to either electrodes and deposit there their electric charges. Thus being freed from the electric energy these then reappear as the usual chemical elements or groups and may then be set free as such, or undergo further chemical decomposition with the electrode or the solution (cf chapter on electrolysis).

The most recent advances in this, deal with the extension of the ionic theory and this is because of the conception of the materialistic nature of electricity. It was naturally anticipated that there would be a corresponding 'positive' electricity as well, when 'negative' electricity was first shown to be material. But later work points to the conclusion that there is only one kind of electricity - 'negative electricity' or as it is now termed "electrons". Thus therefore the theories of electrolysis had to be readjusted and this has been done notably by Sir W. Ramsay

(Presidential Address to the Chemical Society 1908-9) It is now assumed that the elementary atoms are combined with electrons in two ways—with 'active' and with 'latent' electrons. The number of the latent electrons depends upon the maximum valency of the element and the particular valency displayed in a given instance while the active electrons are the cause of the displayed valency and thus of course of the dissociation into ions as well.

N.B. It will not here be out of place to state that in good many cases the ions though naturally one expects still are not simplest possible e.g. many double salts are evidently not dissociated simply into the metals and the acids. For example, if potassium platinumchloride were to be assumed as $2\text{KCl} \cdot \text{PtCl}_4$ then we might expect that, upon electrolysis platinum and potassium would appear at the cathode and chlorine at the anode. However the fact is that the platinum is found liberated together with the chlorine at the anode. Thus the formula of the salt in keeping with its behaviour in solution is more appropriately written $\text{K}_2(\text{PtCl}_6)$ dissociating as.



When a new theory is to be formulated then the usual course is to collect evidence in its favour so as to substantiate the enunciation of it. On the evidence collected the theory is cast and then again to find out whether the statements made are borne out to be true or not, deductions based upon it are drawn and these verified with actual facts. With regard to this electrolytic dissociation theory we will follow the same order.

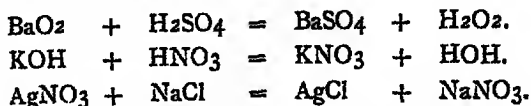
I—Evidence for Dissociation in (Electrolytic) Solutions

(1) Abnormal constants—

The abnormal results got for the boiling point, the freezing point and the osmotic pressure are in themselves clear indications of the increase of the number of particles that have effect in withholding the vaporization of the solvent (molecules) etc.

(2) Chemical reactions in solutions.—

(a) **Simplicity.**—There is a simplicity in the chemical action of the solutes dissolved, upon each other. This strongly suggests previous existence of free separate entities to be able to behave independently. This can be easily seen from the following double decompositions :



These reactions show a simple exchange. The metals interchange places with each other or with hydrogen while NO_3 or SO_4 goes through the reaction as a single unit.

(b) **Rapidity.**—The reactions come about with great rapidity. This indicates that there is very little, if at all, preliminary work to be done, in decomposing these materials into these groups.

This is not the case with non-electrolytes— which are slow, —or from those occasioned by heat. *viz.* KClO_3 .

(c) **Along a particular line of weakness.**—From the breaking of the compounds it appears that there is a distinct line of weakness in the molecules (of electrolytes). $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2 + \text{SO}_4$ while SO_4 acts as a unit.

(3) The law of thermoneutrality.—

When dilute solutions of two soluble salts are mixed and no physical change, such as formation of a precipitate or an evolution of a gas, takes place, there is little or no heat change.

Dilute solution of sodium nitrate NaNO_3 mixed with dilute solution of potassium chloride KCl shows no heat change, but on evaporation a certain quantity of potassium nitrate KNO_3 and of sodium chloride NaCl each is obtained showing the following reaction to have taken place.



If in dilute solutions the various molecules represented in the equation are all parted into independent units, as K, Na, Cl and NO_3 and only in concentrated solutions form any considerable number of molecules, we can see why there should be little evidence of reaction on mixing the dilute solutions although in a concentrated solution the action takes place accompanied by heat change.

(4) The Facts about Electrolysis.—

[The behaviour of solutions towards electricity

(a) Substances which conduct electricity may be divided into two classes

(1) Conductors of the first class in which the passage of electricity is not accompanied by any chemical change, viz, Metals, graphite and alloys. Along them the current simply passes from particle to particle in rapid succession (conduction)

(2) Conductors of the second class in which the passage of electricity is accompanied by chemical decomposition. These are called the electrolytes. In the case of the solution of the electrolyte, the conductivity is much less than that of the metals and the particles of the solute actually move in the solution, so that the electricity is carried by a kind of convection rather than by conduction.

These conductors of the second class—solutions of substances that will conduct the current—are styled as electrolytes

(b) The electrolyte is always decomposed during the passage of the current and the decomposition is called electrolysis

- (c) The two poles A and B in Fig 16 that conduct the electric current are called the electrodes.

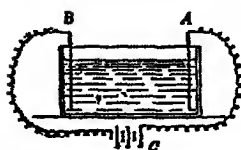


Fig 16

- (i) Positive pole, here A, which brings in the current is called the Anode
- (ii) Negative pole B which leads the current out is called the Cathode.

The current is conducted by the movements of the particles towards the electrodes. These moving particles are called "Ions." (Greek word meaning "to go.")

- (a) Ions moving towards the anode are anions
- (b) Ions moving towards the cathode are cations]

A.—During electrolysis the decomposition products of the electrolyte are deposited on the electrodes or concentrate about them. Thus for example, when copper chloride (CuCl_2) undergoes electrolysis, the copper is deposited on the cathode, while the chlorine is set free at the anode, the products thus appearing at places which may be far apart. Not only the products appear at distant places but they appear instantaneously thus indicating that there is no time lost due to bringing about the decomposition.

B.—It has been found out that if the weight in grams of one equivalent of any metal (or hydrogen) has been liberated, a definite quantity of electricity has been carried through the solution namely, 96,540 coulombs. The quantity of electricity depends merely on the number of the ions and not on their characters.

C.—The combination of copper and chlorine gives out heat.—



The decomposition of it then should absorb heat but instead when it is dissolved in water, a further evolution of heat

takes place equal to 11,080 cals. When this solution is electrolysed there is very little absorption of electrical energy for decomposition of the salt. Thus ·

(1) Appearance of the products at distant poles.

(2) Equal quantity of electricity which an equivalent of every metal carries

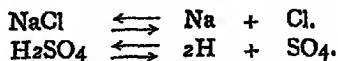
(3) No absorption of electrical energy for decomposition, suggest that in the act of solution there is a decomposition of the character represented in the equilibrium $\text{CuCl}_2 \rightleftharpoons \text{Cu} + \text{Cl}_2$ and that electrolysis does not cause decomposition but depends upon it.

II—Theory of Ionization (electrolytic dissociation).

From the several laws and results found relating to solutions of electrolytes and electrolysis, a theory has been put forth as the theory of "Electrolytic Dissociation" i.e., Ionization. The chief points which this theory asserts are—

(1) Electrolytes form ions in solution.—The electrolytes when dissolved in water no more remain completely as dissolved molecules but these molecules split themselves up into smaller groups of atoms or even to atoms, and these are styled as "ions" from their nature of constant movement.

(2) The ionization of the electrolyte results in an equilibrium.—When any electrolyte dissociates, i.e., ionization takes place, then the ionization does not complete itself but an equilibrium is reached between the molecules decomposing into ions and those ions reforming into molecules again:—



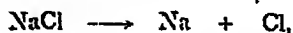
This equilibrium is determined by the influence of chiefly the following three conditions:—

(a) The nature of the electrolyte—Different electrolytes have different degrees of dissociation and of remaining as free ions in solution.

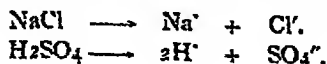
(b) **The nature of the solvent.**—Different solvents have different degrees of ionizing the solutes. Water is the best, and liquid ammonia NH_3 and sulphur dioxide SO_2 come next to it while there are a good many as ether or benzene (as a rule organic liquids) which do not at all ionize the solutes.

(c) **The dilution.**—The ionization percentage increases as the dilution increases. From the kinetic standpoint this increase of ions is quite apparent. Here the dilutions increase the space for movement of the ions. Thus the ions do not come under each others influence so very often as would be the case if the solution is a concentrated one. This want of space would bring them closer and that too oftener together and thus make them reassociate themselves into molecules. Hence dilution increases the ionization.

(3) **The ions are electrically charged.**—The theory of ionization must give some explanation as to the nature of the difference of behaviour of the ordinary molecules and atoms. Ordinary sodium and chlorine atoms cannot be present as such in the equilibrium expressed in



for sodium is a metal which violently decomposes water and chlorine is a gas not much soluble in water and has a pungent odour, whereas sodium chloride forms an odourless and perfectly stable solution. The explanation of this peculiarity of behaviour is this that the ions are considered as bodies heavily charged with electricity and in consequence of these heavy charges they have totally different properties than that of the uncharged atoms or compounds. Each molecule gives rise to two kinds of ions of equal and opposite charges when it ionizes



Since the opposite charges are equal always, the solution on the whole remains electrically neutral. It is by virtue of these charges on movable bodies that the electrolytes conduct the current through the solution

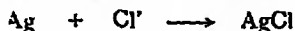
III —Deductions from the theory of ionizations

If the theory as outlined above is to present a correct picture of the conditions existing in a solution of an electrolyte certain logical deductions at once follow —

- (1) Properties of the same ions, whatever their source, must be the same throughout

An ionizing solution will have two independent sets of properties, one due to the molecules and the other due to the ions. All solutions containing a certain ion, say Cl' should have one set of properties, irrespective of the source of that ion. This is found to be true, as for example all soluble chlorides (electrolytes) when treated with silver nitrate AgNO_3 solution precipitate insoluble silver chloride AgCl .

This may be regarded as due to an equilibrium which the Ag' and Cl' -ions tend to set up with AgCl —



This silver chloride AgCl is practically insoluble and as soon as it is formed the solution becomes supersaturated and a precipitate is the result.

- (2) The colour of the solution (due to ions or to molecules) —Since we assume that the ionization is nearly complete in dilute solutions the colour of the solutions must be due to the several ions rather than to the molecules, while in more concentrated solutions the colour of the molecules will predominate. In accordance with this view we find that concentrated solutions of various salts of the same coloured metal have quite a variety of colours while the dilute solutions have the same colour *v.z.*, copper salts have various shades of blue,

yellow and green in concentrated form while the dilute solutions are all pale blue and are not distinguishable in colour

(3) Proportions of the physical constants.—These should be in accordance to the number of ions formed (NaCl , CaCl_2 , H_2SO_4 , FeCl_3 etc.). In dilute solutions in which the ionization is regarded as more or less complete, the effect on boiling point or freezing point or osmotic pressure should reach a maximum value. Thus in sodium chloride NaCl it should be double, in calcium chloride CaCl_2 it should be triple and in ferric-chloride FeCl_3 it should be four times and so on, than that found with regard to non-electrolytic solutions such as of sugar. In a general way it can safely be said that such are the real facts that have been found out with regard to such solutions.

The theory of ionization or dissociation is a broad theory and gives us a working picture of the peculiarities of the solutions of electrolytes. It is not completely satisfactory but a great many facts can be represented much more simply in terms of this theory. It has done good work and promises to do more. Gravitation Theory of Newton in the earlier days was opposed in a similar way although now an opponent of gravitation theory would be considered unreasonable. This theory has been and may be still modified but as it is, it gives us a good working hypothesis and hence better it is adopted.

CHAPTER XIV

Neutralization & Salt Formation.

While discussing about electrolytic dissociation we have seen that salts, bases and acids which were styled as electrolytes ionize when thrown into water. Similarly we have also seen that the ions formed in the case of acids always contain hydrogen ions, and in the case of bases, always contain the hydroxyl ions. These ions have opposite kind of electricity on them, and thus must attract each other. Thus when an acid and a base are brought together in solution, the reaction always consists in the union of H' and OH' and thus of nullifying the effect mutually, with the formation of water, a neutral substance which is extremely little dissociated when formed.



This reaction is called neutralization.

Before discussing this further let us first consider, what an acid is and a base is from the ionic point of view.

I Acids

If the formulæ of the different acids are examined, their inspection tells us that they all contain one element common and that is 'hydrogen'. If we still extend our inspection further to other compounds such as sugars, oils, fats, waxes then we find here also the same element common, but these still are not acids.

Acids as a class show :

- (1) Sour taste – atleast those that are appreciably soluble.
- (2) Reaction to litmus. (Blue to red).
- (3) Act chemically on bases
- (4) Conduct electricity (when in aqueous solution).
- (5) Form hydrogen ions H^+ .

From the above properties which we have seen to be due to the dissociation, and formation of H^+ ions; an acid can be defined as : “ A compound which produces H^+ ions when dissolved in water ” Because as just said all the attributes found for an acid are nothing but the attributes of the H^+ ion; and the rest of the part of the molecule does not play any part in the acidic behaviour.

A. Some important characteristics of H^+ ions:

(a) The most important and outstanding property of the H^+ ion is the neutralization of OH^- ion and eventual formation of H_2O which is very little ionized. Hence whenever any compound giving OH^- ions is brought in contact with H^+ ions of a solution of an acid they neutralize each other and their individual properties disappear.

(b) Whenever a metal (with a few exceptions) comes in contact with the H^+ ions of an acid, the metallic atoms pass into solution as ions and hydrogen is liberated as a free gas.

B. Basicity of Acids. As already seen (p. 133) basicity of an acid is its power of neutralizing a base, and depends usually on the number of hydrogen atoms in the molecule. But in the case of some inorganic and almost all organic acids the

mere number of hydrogen atoms in the molecule leads to wrong conclusions. Because :—

Acetic acid CH_3COOH is mono-basic

Tartaric acid $\begin{array}{c} \text{OH} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{OH} \end{array}$ is dibasic

Citric acid $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{HO}-\text{C}-\text{COOH} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{H} \end{array}$ is tribasic

In these cases as the basicity is not in accord with the number of hydrogen atoms present, the formulæ are represented by separating those hydrogen atoms only which get ionized. Thus

Acetic acid $\longrightarrow \text{H.C}_2\text{H}_3\text{O}_2.$

Tartaric acid $\longrightarrow \text{H}_2 \text{C}_4\text{H}_4\text{O}_6$

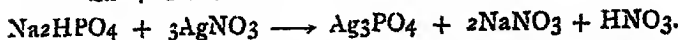
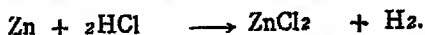
Citric acid $\longrightarrow \text{H}_3 \text{C}_6\text{H}_5\text{O}_7.$

Radical Here we distinctly see that the acids form two parts, one of acidic hydrogen and the others which through the chemical reactions maintain their individual grouping and character. These are called radicals (Ramus = branch) Thus

When an atom or a group of different atoms which goes through reactions undisturbed acting as units like the above group $\text{C}_2\text{H}_3\text{O}_2'$ of acetic acid or the group SO_4'' of sulphuric acid, especially when they can play the role of an ion, are called radicals.

or

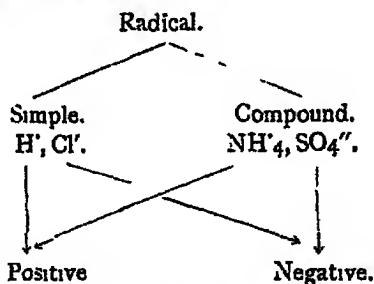
Any portion of a molecule whether it consists of a single atom or of a group of atoms which is capable of being detached and transferred to some other molecule :



Compound radical: Group of atoms acting like a single atom and which enters unchanged into a number of compounds is called a compound radical. We do not here want to enter into the question of their existence or non-existence in the free state as it is of no practical value.

Thus a complete definition for a radical is :

When an atom or a group of atoms of the same kind or of different kinds acts or goes through reactions undisturbed all along and which is capable of being detached and transferred to some other is called a radical



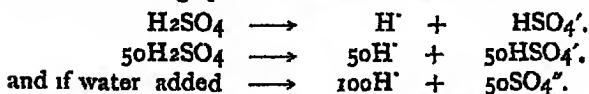
These radicals may be either (1) positive or negative *e. g.* Na^+ , Cl^- , NH_4^+ , NO_3^- etc. or (2) may be mono, di, tri, etc.-valent ones and these are capable either of replacing or of combining with others in a reaction *e. g.* Ca^{++} , PO_4^{---} , etc.

C. Strength of an acid: The strength of an acid means the property of its activity at a particular concentration and dilution. This property is varying in different acids. Since the acid properties are wholly the properties of the H^+ -ions, that acid would be the strongest which will give the largest number of H^+ -ions at a particular time and dilution. This number of H^+ -ions cannot be judged from the formula, for

ionization is always an equilibrium and the concentration of the H^+ -ions depends not only upon the number of hydrogen atoms in the molecule of the acid of a given solution, but also upon the percentage of the molecules which are ionized when equilibrium is reached.

D. Ionization of di- and tri- basic acids —

The ionization is a process that always takes place in stages and hence in moderately concentrated solutions the ionization is largely of the first order as :—

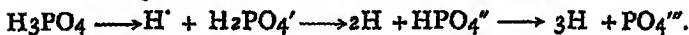


i. e. in dilute solutions a second stage is reached as —



Hence sulphuric acid behaves as a weaker acid than hydrochloric or nitric acid in moderately concentrated solutions

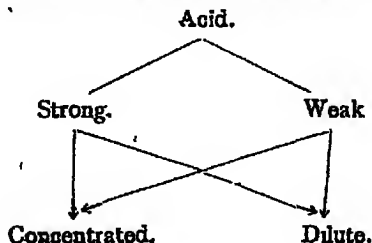
With regard to a tribasic acid it is as follows :—



Non-Ionizing solvents There are many solvents in which atleast some of the acids are soluble and these, if all traces of water are absent, do not show any ionization.

N.B. From C and D it is evident that acids frequently behave differently in different dilutions and thus —

- (a) A strong acid may be concentrated as well as dilute,
- (b) A weak acid may be concentrated as well as dilute.



II Bases.—

Bases are compounds which in composition are made up of some metallic element (radical) in combination with OH (hydrogen and oxygen) Many of them are insoluble in water and when soluble show —

- (1) Soapy feel and brackish taste.
- (2) Reaction to indicators (Red to blue)
- (3) Act chemically on acids
- (4) Conduct electricity.
- (5) Form hydroxyl (OH') ions.

From this a base may be defined as "a compound that produces OH'-ions when (dissolved in water)" in solution.

Some important characteristics of OH'-ions

(1) The most important characteristic property is the neutralization of H'-ions of an acid together with the eventual formation of (neutral) H_2O which is practically undissociated.

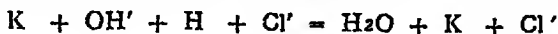
(2) Acidity of the base depends upon the number of hydroxyl groups that each molecule has. When the molecule can furnish one hydroxyl *e.g.* KOH, it is mono-acidic, if two *e.g.* $Ca(OH)_2$, it is diacidic and so on.

(3) Strength of the base The strength of a base is not a fixed property but is varying in different bases As this property of a base depends upon the number of hydroxyls that are available at a particular time in a particular dilution, that base will be the strongest which will give most OH'-ions in solution.

(4) Ionization of di-acidic and tri-acidic bases : Just as in the case of the di- and tri- basic acids so also in the di- and tri- acid bases the ionization takes place in stages

C Salts

When an acid and a base are brought together they nullify the properties of each other on account of the contrary properties of each of them and form water, i.e. the hydroxyl ions of the base and the hydrogen ions of the acid neutralize one another. The remaining positive and negative ions whose electrical charges are equal and always balancing each other, then set up their own equilibrium thus :—



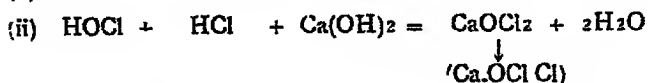
Thus when the solution becomes saturated with the molecular members of the equilibrium, here, potassium chloride KCl, either because of the limited solubility or on account of the evaporation of the solvent, the excess is thrown down in the solid form and this then is known as a salt. Hence a salt may be defined as "A product got by the neutralization of an acid and a base with eventual removal of water."

Properties of salts As in the case of acids or bases there is no one common ion characteristic of the salts and hence there is no set of properties as in the case of acids and bases, but as a rule they are —

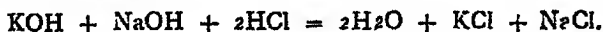
- (1) Electrolytes : i.e. conductors of the second class,
- (2) With a varying solubility,
- (3) And in ionization much more the same (why ?) In short they are strongly ionized
- (4) Nearly all of them are solids and most of them also are colourless.

Different kinds of salts. Ionization is an act which takes place in stages and thus we may neutralize either an acid or a base in stages, and thus may get either H or OH'-ions still remaining unneutralized giving rise to salts which have in their molecular formation either hydrogen or hydroxyl still present unneutralized. These semi-neutralized salts are called

either acid or basic salts according to the presence of H or OH radicals. Similarly if either one molecule of an acid (dibasic) or a base (diacidic) is neutralized by two different bases or acids, then we get what are termed "mixed salts" Thus.



N.B. A mixed salt is not to be confounded with a mixture of salts, thus —



On removing water a mixture of the different molecules of potassium and sodium salts will come down

Hydrogen salts Now as we attribute acid properties to H-ions which exist in solution, then wherever they are not formed (i.e. either in undissociating solvents or in the solid form) say solid oxalic acid, liquid nitric acid or gaseous hydrochloric acid (gas), we should not get acid properties, and so is really the case. These and similar compounds are called "hydrogen salts"

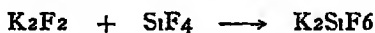
Double and Complex Salts

So far we have considered the different cases of compounds formed by the neutralization of acids and bases brought together in equivalent or different proportions. But at times even salts already formed, if are brought under the influence of each other, they interact not as in the double decomposition, but form a sort of association which may lead to either complete amalgamation of the two compounds resulting into absolutely different properties or may be of a partial type resulting into mere juxtaposition of the different molecules in the new molecule formed. The first type is called the "Complex Salt" and the second one the "Double Salt"

Double Salt When a solution of one salt (potassium sulphate) is mixed with a solution of another (aluminium sulphate) and if these solutions are of a stated concentration, then on evaporation of the mixture it often happens that instead of getting one or the other salt crystallized out, both the salts come down together with the formation of so to say one compound. Here in the above case instead of potassium sulphate or aluminium sulphate coming down in separate crystalline forms, both of these come down together as potassium-aluminium-sulphate with a fixed quantity of water of crystallization. Similar is the case with $3\text{NaF} \cdot \text{AlF}_3$, $2\text{KF} \cdot \text{SiF}_4$, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ etc.

When any of these salts is dissolved in water the solution acts as if it contained a mixture of the two salts. Thus, say if Carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is dissolved in water the solution behaves as if it contained a mixture of potassium and magnesium chlorides, both of them are freely ionized. Reactions for all the different ions: *e.* K^+ or Mg^{2+} or Cl^- are got in the analysis. "Thus a salt of this kind which in solution decomposes into its constituent salts and then gives reactions for their individual ions is called a Double Salt."

Complex Salt Similar to the double salts when solutions of different salts are mixed, at times instead of getting a salt showing properties of the original substances, quite new properties are found to be given rise to in the new compound separated. Thus if potassium fluoride K_2F_2 and silicon fluoride SiF_4 solutions are brought together we get a compound



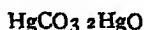
From the above analogy we expect to get reactions of K^+ , Si^{4+} and F^- but nothing of this kind happens. The silicon and fluorine seem to have lost their properties and we get quite a new radical SiF_6^{2-} instead. Same is the case with K_3HgCl_4 , $\text{Ag}(\text{NH}_3)_2\text{Cl}$. "Compounds of this kind which yield ions other than those of the salts from which they may be formed are called Complex Salts."

Thus in all we have six varieties of salts.

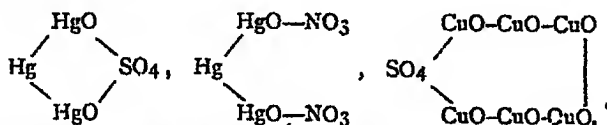
(1) Normal (some times wrongly called neutral) NaCl , CaCl_2 .

(2) Basic Cu OH Cl , $\text{Bi NO}_3 (\text{OH})_2$
 $\text{Bi}(\text{NO}_3)_2\text{OH}$

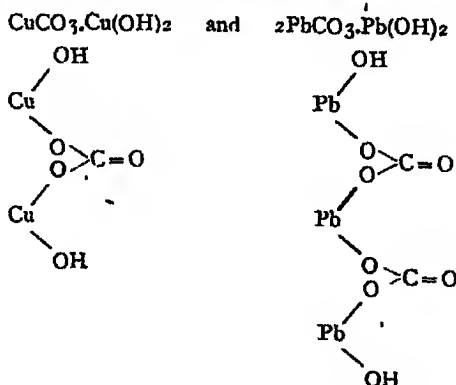
Again those salts where the quantity of the metal or the compound radical exceeds the number of atoms of the displaceable hydrogen in the acid e.g.



If we conceive a radical 'metallyl' the formation of such salts may be accounted for thus —



Again these basic salts formed by dibasic acids and diacid bases or dibasic acids and tribasic acids may be explained as —



(3) Acid. NaHSO_4 ; NaHCO_3 .

(4) Mixed. Ca.OCl.Cl , KNaSO_4 .

Mixed salts may be of two kinds —

(1) (a) one base and different acids

(b) one acid and different bases

(ii) The term mixed salt is however usually applied only to those salts in which two different metals replace the hydrogen in one molecule of an acid

(5) Double... .. $\text{Al}_2(\text{SO}_4)_4.24\text{H}_2\text{O}$

(6) Complex $\text{K}_4\text{Fe}(\text{CN})_6$, K_2HgCl_4

CHAPTER XV.

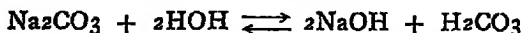
Hydrolysis.

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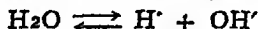
It is a very common experience that when we take equivalent quantities of acids and bases, though we expect to get salts which should show neither any acid nor any basic reaction to litmus, but on the contrary should be absolutely neutral in reactions, still we realise that what we expect is not always the case. We should get what should really be called "Neutral salts" as opposed to acid and basic salts. But we know that we cannot call them 'neutral' and have to call them "Normal Salts", because they do not necessarily show the same reaction though they are formed with equivalent quantities of acids and bases. What is the reason for such a peculiar behaviour on the part of these normal salts? Does this mean that the reaction of neutralization does not complete itself; or does it mean that a new kind of either an acid or a base is given rise to? If we hold the first view, then the ionic theory is defective. Even if the latter statement is accepted still how would this help us to get only one kind of reaction *i. e.* acidic or basic? Of course here we may assume that either the acid or the base of the original products does not dissociate completely and thus giving chance to the other to show its chemical reaction. All this is quite alright when a salt is being formed and the formation of H_2O molecules from the hydrogen and the hydroxyl ions leaves only the other ions to combine with each other. These ions, as we know from the ionic dissociation, have themselves no reaction on litmus, and hence if the salt is formed once, we should have no reaction on litmus if we dissolve the salt in water (ionizing solvent).

But we do find that normal salts in solid condition when dissolved in water give often reaction to litmus. This clearly goes to prove that an acid or a base is once more regenerated.

How is this to be accounted for, unless we agree in supposing that water itself acts as a compound or a salt giving rise to double decomposition in the reaction with the dissolved solid. Thus —



But this presupposes that H_2O molecules are not undissociable as was supposed when we discussed about neutralization. There we regarded water merely as a solvent and the possibility that it is electrolytically dissociated had not been taken into account. There is however a considerable amount of evidence to the effect that water itself is ionised, though to a very slight extent according to the equation



because the conductivity of pure water, though very slight indeed, is just perceptible. This clearly shows that water is very slightly split up into hydrogen and hydroxyl ions as expected above.

From the foregoing facts it is evident that water is both an acid and even a base, as it contains both hydrogen and hydroxyl ions. Should either of these ions be removed wholly or in part by a reaction between them and some other substance dissolved in water, more water molecules ionize to keep the concentration at the equilibrium stage.

Having accepted the fact that water can act either as an acid or as a base as the conditions would demand, it becomes quite obvious as to the behaviour of the normal salts in solution. It is a simple case of double decomposition, where the water acts either as a competing acid or a base with the basic or the acid radical of the salt. We know that if two acids are allowed to compete for the same base, the latter distributes itself between the acids in proportion to their activities, and we also know that the ratio of the activities of the two acids is the ratio of the extent to which they are ionized. Now let us consider the cases of the different type of salts.

(1) Salt of a strong base and a strong acid. In the case of a salt of a strong acid and a strong base, such as sodium chloride, we cannot conceive that such a weak acid as water would take an appreciable amount of the base (or vice versa) and the available experimental evidence quite bears out this expectation.

In other words an aqueous solution of sodium chloride contains only Na^+ and Cl^- ions and non-ionized sodium chloride, in appreciable amounts and is therefore neutral to litmus.

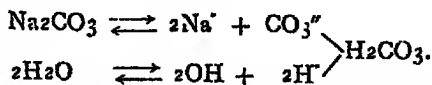
(2) Salt of a strong base and a weak acid. In the case of a salt of a strong base and a weak acid, such as sodium carbonate, water as an acid is comparable in strength to carbonic acid and there is therefore a distribution of the base between the acid (H_2CO_3) and the water (the acid H.OH) according to the equation



the proportion of sodium carbonate and sodium hydroxide depending upon the relative strengths of water and carbonic acid under conditions of the experiment. From the equation it is evident that sodium hydroxide and carbonic acid must be present in equivalent proportions, and since the hydroxide is much more highly ionized than carbonic acid, the solution contains an excess of OH^- -ions, and must therefore be alkaline which is actually the case.

This above case can be also explained by another way of argument, and it is thus :—

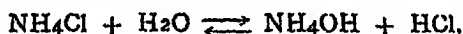
Sodium carbonate is the salt of a weak acid and a strong base and is fully ionized :



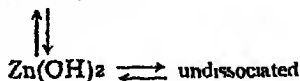
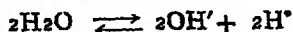
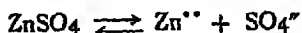
The carbonate ions at once unite with any hydrogen ions they chance to encounter, to form non-ionized molecules

of carbonic acid as this is a very weak acid *i. e.* the least dissociated. This will go on till the concentration of the carbonate ions has been very materially reduced, and a corresponding number of hydrogen ions removed. Equal numbers of sodium ions and hydroxyl ions, the original partners of the carbonate and hydrogen ions respectively, will remain in the solution. Owing to the presence of these hydroxyl ions the solution will turn red litmus blue, and generally speaking, behaves very much like the solution obtained by dissolving caustic soda in water.

III. Salt of a weak base and a strong acid. In the case of salts of weak bases and strong acids analogous considerations to the above one apply to the action of water. Let us take the case of ammonium chloride. Although water is much weaker than ammonia as a base yet the salt is slightly decomposed by water :—



and as hydrochloric acid is much more highly ionized than the hydroxide, the solution contains an excess of H^+ -ions and is therefore acidic. Again suppose we dissolve zinc sulphate, a salt of a weak base and a strong acid, it is fully ionized, but the metallic and hydroxyl ions speedily unite to form non-ionized molecules of the metallic hydroxide, and at the same time hydrogen ions gradually accumulate, so that the liquid is able to turn blue litmus red, or otherwise to act as an acid.



As can be easily foreseen, salts of weak acids and weak bases are hydrolysed (decomposed by water) to a still greater extent under equivalent conditions than those belonging to the types just considered; and thus when both the acid and the

base are weak, the processes which have just been explained will mutually support one another and appreciable quantities of the undissociated acid and base will result. The production of an excess of hydroxyl and hydrogen ions will on the other hand be diminished, since the cations of the base will use up one, and the anions of the acid the other.

Thus in short we have seen that water plays a very important role in the behaviour of salts, and so to say by acting either as an acid or as a base, brings about double decomposition or in other words decomposes a salt. This decomposition of a salt by means of water molecules is commonly termed "Hydrolysis" (hydro = water; lysis = loosening).

N. B. —

(i) As the concentration of H^+ and OH^- ions of water is practically constant on dilution, whilst the H^+ ion concentration of the competing acid, or the OH^- ion concentration of the competing base diminishes with dilution, the hydrolysis of salts of the first two types considered, increases on dilution. Further as the ionization of water increases rapidly as the temperature rises and the strength of the other acids and bases is only slightly affected by increase of temperature, the hydrolysis of salts is markedly increased by raising the temperature.

(ii) Salts of a strong base and a weak acid give on hydrolysis alkaline reaction *e. g.* Na_2HPO_4 , K_2CO_3 Sodium phosphate (secondary) although an acid salt is still basic in reaction.

Similarly a solution of a salt of a weak base and a strong acid becomes acidic on hydrolysis. *e. g.* $CuSO_4$, $Al_2(SO_4)_3$. These salts are normal salts, but are acidic in character though there is no acid present in them : *e.* though they are not acid salts

(iii) Whilst judging the probable litmus reaction of a salt it is not only sufficient to know and remember as to the strength of the original acid or the base, but it is absolutely essential to remember the acidity or the basicity of the original

base and the original acid. For we know that dissociation takes place in stages and during this, it is almost invariably the case that the ionization in the first stage is much greater than the second and very much greater than in the third stage. Thus in the case of phosphoric acid, it is a fairly strong monobasic acid, a much weaker dibasic acid, and as a tribasic acid it is extremely weak, and from this it follows that .—

- (1) NaH_2PO_4 is quite a stable salt.
- (2) Na_2HPO_4 is slightly hydrolysed.
- (3) Na_3PO_4 is almost completely hydrolysed

(1) $\text{NaH}_2\text{PO}_4 \longrightarrow$ almost neutral

(2) $\text{Na}_2\text{HPO}_4 \longrightarrow$ slightly basic.

(3) $\text{Na}_3\text{PO}_4 \longrightarrow$ Strongly basic.

(iv) It should be remembered that the strong acids are hydrochloric, sulphuric and nitric, and strong bases are potassium, sodium and calcium hydroxides. It is now quite evident why salts of alkalis : *e.* the metallic radicals of the last group in qualitative analysis must be either giving neutral or basic reaction and if the solution gave an acid reaction in the preliminary tests, it can never be one of the alkali metals.

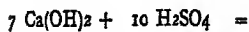
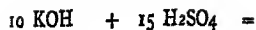
Questions

(1) What will be the reaction to litmus for the solutions of . (1) Ferric chloride, sodium sulphide, copper nitrate, sodium borate, calcium sulphate, ammonium carbonate.

Give reasons for your answers.

(2) Complete the equations





Show by ionic equations as to how you arrive at your results and show what will be the reaction to litmus of the above mixtures.

(3) Alum is used as a very efficient water purifier in large storage tanks and reservoirs. It is said that this purifying property depends upon the hydrolysing influence of water on the salt. Explain how this happens.

CHAPTER XVI.

Electro-Chemistry.

Electrolysis.

Electro-chemistry is chemistry as concerned with electricity. It deals with the study of the phenomena by which chemical actions give rise to electricity and by which electric current produces chemical actions.

(1) Every chemical action produces electricity.

When a base and an acid are brought together and when they combine there is electricity produced, the base taking '—ve' electricity and the acid '+ ve' electricity. The same phenomenon occurs when a metal is dissolved by an acid but as the two electricities combine together we do not perceive it. To make it apparent the combination should take place outside the system and this is brought about by the "current" or the 'circuit'.

(2) Electric discharges —The electric spark may provoke a number of chemical reactions when passed through gases or vapours. This is probably due to the high temperature which is reached after the discharge.

In the present chapter we deal with the reactions and quantities that are produced when an electric current is made to have its effect on solutions. The solutions only of a certain type of compounds are decomposed by the current and the products of decomposition either are deposited in or are evolved out of the solution. This kind of reaction is called electrolysis. Thus this kind of decomposition is defined.

Electrolysis (Electron=amber, and lyo=dissolve) is the act of decomposition of an electrolyte into its radicals when an electric current is passed through it.

Electrolytes are, as already said, second class conductors, *i.e.*, in the case of the conduction of a current by an electrolyte it will be noted that an actual transference of the material takes place, accompanied by chemical changes; whereas in ordinary conduction (First class) as in the case of metals, neither transfer of material nor chemical changes occur.

(The aqueous solutions of acids, bases and their salts are in general good electrolytes, though some conduct much better than others. There are also some non-aqueous solutions which are electrolytes but they are relatively unimportant.)

Faraday's Laws of Electrolysis: Throughout the study of electrolysis, a striking relation between the electrolytic behaviour and the chemical behaviour of various substances will be observed. This suggests a very close relation between electricity and all chemical activities. Faraday established by experiments the following two laws, which are known respectively, as Faraday's First and Second laws of electrolysis.

First Law. The mass of a substance deposited or liberated at an electrode is proportional to the quantity of electricity that has flowed through the electrolytic cell

or

For the same electrolyte, the amount of chemical action is proportional to the quantity of electricity which passes.

Second Law: The mass of a substance deposited is proportional to the chemical equivalent of the ion *i.e.*, proportional to the atomic weight of the ion divided by its valency.

or

The quantities of the substances liberated at the electrodes when the same quantity of electricity is passed through different solutions, are proportional to their chemical equivalence.

The second law therefore states that $\left[\frac{\text{at. wt}}{\text{valency}} = \text{chemical equivalent} \right]$ when the same quantity of electricity is passed through solutions of such electrolytes as Na_2SO_4

AgNO_3 , CuSO_4 , AuCl_3 , the relative amounts of hydrogen, oxygen and the metals liberated are according to what follows : If the experiment is arranged by taking four electrolytic cells A, B, C and D containing the solutions indicated, and placed in series,

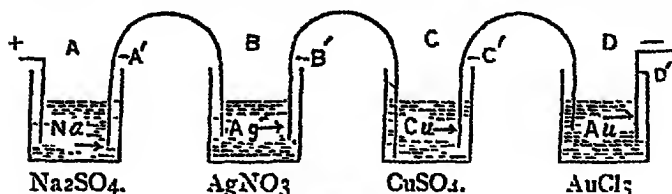


Fig 16

the same current consequently passes through each, and hence the same amount of charge must be carried through cell B by silver ions as through C by copper ions and so on.

Since the current is flowing to the right and since the metal ions are positive and therefore travel in the direction of the current, it is evident that, the electrodes A', B', C' and D' will gain weight due to the decomposition of the metallic ions.

For these reasons these electrodes may be called 'gain' plates. If the metals are all monovalent (valence 1) then the same number of atoms of each would be deposited and the gain of weight for the different gain-plates would simply be proportional to the respective atomic weights of the metal ions deposited on them by the current. But since the valencies of different metals are not the same, the amounts of different elements—metals—deposited would be in proportion to the fractions of their atomic weights or in short, in proportion to their equivalent or combining weights. As here.—

Electrolyte : Na_2SO_4 , AgNO_3 , CuSO_4 , AuCl_3

Electrochemical equivalent. $\text{H} = 1$, $\text{O} = \frac{16}{2}$, $\text{Ag} = \frac{108}{1}$, $\text{Cu} = \frac{63.6}{2}$,

$$\text{Au} = \frac{197}{3}.$$

Therefore the quantities liberated will be according to the above in the ratio of

H. O. Ag. Cu Au :: 1 : 8 : 108.5 : 8.6566 or again it is found that though the elements in the different electrolytes be the same still the quantities liberated depend directly upon the equivalence and not upon the atomic weight which is a fixed quantity while the other is not. Thus in figure 17 we find that the

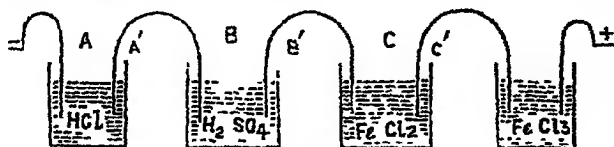


Fig 17

quantities of hydrogen evolved are the same, yet the quantities of iron deposited are different and these are in the ratio of $\frac{56}{2} = \frac{56}{3}$ according to the valency of iron which is divalent in one case and trivalent in the other case.

Hence the above law (second) may be stated rather differently as follows —

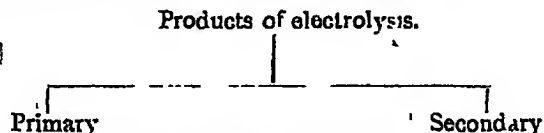
“The electro-chemical equivalents (the proportions of different elements set free by the same quantity of electricity) are proportional to the chemical equivalents”.

Thus as seen above, under the influence of an electric current the salt undergoes electrolysis and is resolved into radicals of two kinds *viz*,

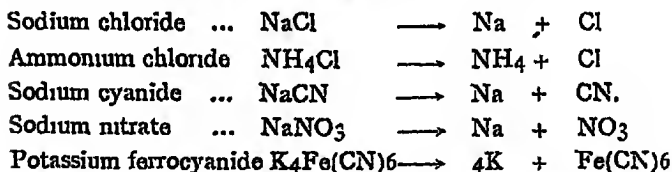
- (i) The positive or metallic radical like Na^+ , Ca^{++} , NH_4^+ etc
- (ii) The negative or non-metallic radicals like Cl^- , CN^- , SO_4^{--} , NO_3^- etc

The positive radicals as seen are carried with the current and liberated at the cathode A (Kata = down, hodos = a way) i. e., the electrode where the current leaves the liquid; the negative radicals are carried in the opposite direction and are set free at the anode (ana = upwards, hodos = a way) where the current enters the liquid

When electric current is passed through an electrolyte the products that come out at the end as a result of electrolysis are the result of either the direct decomposition or may be given rise to, by the products formed by the first decomposition of the electrolyte. The first kind of products are called primary, and the second kind are called secondary.



In the case of a binary salt, such as sodium chloride the primary products of electrolysis are Simple Radicals containing only one element such as sodium or chlorine, but in other compounds these are replaced by Compound Radicals containing more than one element, as in the ammonium salts, cyanides, nitrates, ferrocyanides etc.



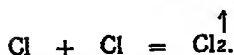
When the primary products are liberated at the electrodes they frequently undergo decomposition or chemical change, giving rise to secondary products, by interacting

- (a) with one another, or
- (b) with the electrode, or
- (c) with the electrolyte,

(a) **Polymerisation.**—When molten silver chloride is electrolysed between a silver cathode and carbon anode



the silver atoms appear, perhaps without chemical change as metallic silver but the chlorine atoms unite in pairs to form molecules of chlorine gas

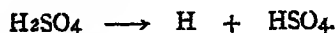


So also when a cyanide is electrolysed we have at the anode the formation of cyanogen gas from pairs of cyanogen radicals,

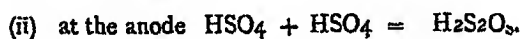
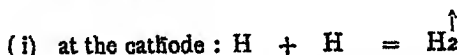


Similarly the electrolysis of fairly strong sulphuric acid gives hydrogen gas at the cathode and per-di-sulphuric acid, as shown in the following equation :—

Primary decomposition —



Secondary change :—



per-di-sulphuric acid

(b) Attack on the anode :—In other cases the anode is attacked by the negative radical, as for instance,

(i) when silver nitrate is electrolysed in a silver voltmeter : $\text{NO}_3 + \text{Ag} = \text{AgNO}_3$

(ii) when copper sulphate is electrolysed between copper plates : $\text{SO}_4 + \text{Cu} = \text{CuSO}_4.$

(iii) when lead nitrate is electrolysed between lead plates $2\text{NO}_3 + \text{Pb} = \text{Pb}(\text{NO}_3)_2.$

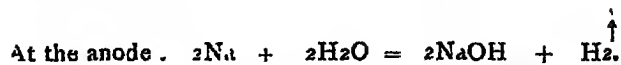
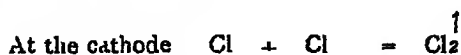
In these cases the negative radicals dissolve from the anode just as much metal as is deposited at the cathode, so that at the end of the action the composition of the solution is unchanged, but a transfer of the metal has taken place from the anode to the cathode.

(c) Interaction with the Electrolyte :—In other cases the primary products interact with the electrolyte, as at the cathode in the electrolysis of the brine

Primary decomposition —

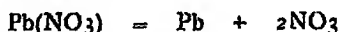


Secondary changes

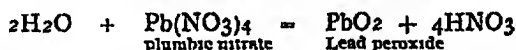


or at the anode in the electrolysis of lead nitrate between platinum electrodes, where plumbic nitrate is perhaps an intermediate stage is the production of lead peroxide

Primary decomposition



Secondary changes at the anode



Now so far what we have considered in the different changes that take place in an electrolyte, due to the passing of the electric current is this, that in all these cases we presuppose the very existence of the different radicals. The current that is being passed is doing only the directing of these radicals to the different poles. In all these cases we have always kept in mind that the poles of the battery have either (firstly) no effect on the electrolyte, or (secondly) their exchange may not affect the individual reactions. But such is not at all the case.

Poles are not only affected as the result of the secondary reaction of the electrolysis, but these themselves have a very great influence on the decomposition of the electrolyte.

Everybody must have noticed in the very common experiment of dissolving copper sulphate in water that if the blade of a pen-knife is used as a stirrer, a fine reddish deposit of copper

appears on the blade of the knife, though there was no electric current as such utilized, just as in electrolysis, while if a pencil is used no deposit of any kind appears on the pencil.

Just as in the above case iron knife and copper solution behave, similarly other metals also behave in the same way and displace one another, of course, not indiscriminately but according to a certain gradation or order depending upon the individual strength of displacing or of being displaced. These metals if they are arranged according to their displacing power are displaced in the following order —

- (i) $Mg \rightarrow Al \rightarrow Mn \rightarrow Zn \rightarrow Cd \rightarrow Fe \rightarrow Co \rightarrow Ni \rightarrow Sn.$
- (ii) $Pb \rightarrow Bi \rightarrow Cu \rightarrow Hg \rightarrow Ag \rightarrow Pt \rightarrow Au.$

Again it is also noticed that if any of the metals of the first (i) group say Zn, is treated with a dilute acid say hydrochloric, then the reaction produces an electric current of a certain voltage. The voltage of the current is not found to be the same with the different metals, but is found to increase or decrease as the metal be above —Al,—Mg,— or below — Fe, Co — zinc in the above order. It is thus possible to arrange the elements in a series representing the potential difference in volts which is developed between the metals and the solutions of their salts.

The order here as in the above case is found to be virtually the same, and is called 'Electrochemical Series' of the elements where non-metals are also included

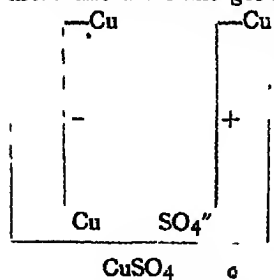
- (i) $K - Na - Ba - Sr - Ca - Mg - Al - Cr - Mn - Zn - Fe$ etc
- (ii) $H - Bi - Cu - Hg - Ag - Pt - Au ;$
- (iii) $Si - C - B - N - P - S - I - Br - Cl - O - F.$

Just as the metals have a tendency to displace or to be displaced by one another on account of their difference of potentials, similarly metals even if they are brought in contact with the solution of their own salts will usually go in solutions, of course, till an equilibrium is established. This tendency either

of the metals displacing one another or going in solution or even in some cases of being deposited is due to the tendency of these metals to become ionic. This tendency is regarded as a "Solution Pressure" which drives the ions of the metals into solutions no matter whether the ions are of the same valency and of the same kind.

Herein the number and kind of the valency of the ion is not the differentiating factor but it is the 'degree of tenacity' of assuming and holding the electric charge. This degree of tenacity is called 'Electro-Affinity of the element.' On account of this (1) K and Na, (2) Ca and Mg, (3) Cu and Hg, (4) C and S, or (5) I and Cl even though they have the same and also similar valencies still, the first elements of the pairs will be displaced by the second (element) ones.

On account of these facts if we take the same solution say copper sulphate, and electrolyse it by a current passed through poles of (1) copper, (2) platinum and (3) carbon, respectively then in the first case, copper from the positive pole will go in solution more and more and get deposited on the negative pole and



thus the concentration of the solution will remain the same while the positive pole will get diminished, but the loss in weight here will be counter-balanced by the gain in weight by the negative pole on which the copper ions get neutralized and deposited.

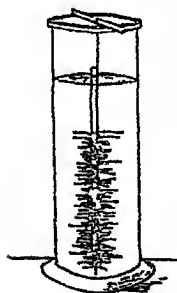
But in the second and the third case as we can see from the 'electro-affinity' series that copper is higher than either platinum or carbon, no element of the pole can go in solution in this copper solution, and thus when neutralization of the electric charge takes place at the different poles the concentration of the copper sulphate solution gets weakened by the deposition of copper at the negative pole without any equivalent

addition to substitute the loss. So in the end the result would be that all copper from the solution will be removed and the sulphuric acid will be left out, but at the same time oxygen will be given out at the positive pole due to the action of SO_4 upon water:—



In all these considerations it must have been noticed by this time that the strength (voltage) of the current is assumed to be a fixed one. But it must be clearly borne in mind that change in the voltage of the current also brings about alterations in the reaction.

The 'solution tension' of the metals is best demonstrated when a strip of zinc is dipped in a solution of lead nitrate. The solution tension of zinc is greater than that of lead, so that when a strip of zinc is dipped in a lead solution it forces the



zinc 'ion' into solution and becomes negatively charged. The lead ions are therefore attracted by the zinc and discharged, i.e., lead is precipitated from the solution. The process stops when all the lead of the solution has been precipitated provided when zinc is in excess. The precipitated lead adheres to zinc in the form of dendritic crystalline mass, which formation is known popularly as 'lead tree' Fig 18

Fig 18

Not only the metals but every solid, like sugar, when brought in contact with water has a tendency to pass into solution. From the analogy with metals and solutions we may say that every solid has a definite solution tension. The solution tension in the case of soluble solids is best illustrated in the formation of metallic silicates, by a familiar experiment. 'Silica Garden'

A litre beaker is filled with a solution of sodium silicate (sp. gr. 1.1) and crystals of say cobalt nitrate, cadmium nitrate,

Secondly we know that the quantities of the liberated products will be in their equivalent ratios from the law of Faraday.

∴ If copper deposited is 63.6 grms in weight the several quantities of hydrogen, chlorine and oxygen will be in proportion to the equivalents of copper.

$$\therefore \frac{\text{Equivalent of oxygen}}{\text{Equivalent of copper}} = \frac{\text{wt. of O deposited}}{\text{wt. of Cu deposited}}$$

$$\therefore \frac{8}{31.8} = \frac{\text{wt of O deposited}}{63.6} = 16 \text{ grms.}$$

Similarly for hydrogen and chlorine which are respectively 2 grms and 71 grms.

(2) The same current is passed through cells containing solutions of (a) HCl, (b) CuSO₄ and (c) Ag₂SO₄. What products are obtained in each case? If one gram of silver is obtained from silver sulphate, what are the weights of the other products Cu = 63.6.

(3) An electric current is passed simultaneously through aqueous solutions of the following: (a) KI, (b) CuSO₄ and (c) conc. HCl. What substances and what quantities of each will be formed when the current passed was 96,540 coulombs.

(4) How many coulombs of electricity would be required to deposit 1000 grms. of copper from a solution of cupric salt? One coulomb will deposit 0.001118 gm. of Ag.

(5) A current passes simultaneously through acidulated (with sulphuric acid) water, a solution of copper sulphate and of silver nitrate. What substances are produced in each case and how many grams of each, in the time that 10 c. c. of hydrogen at N T P are liberated from water.

(6) Sodium sulphate and copper sulphate solutions are placed in the same circuit. It is found that by the time 500 c c of hydrogen at 27° and 740 mm were evolved in the first cell, 1.218 grms. of copper was deposited in the second cell. Determine the equivalent weight of copper

CHAPTER XVII

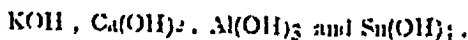
Valency.



Meaning of the term. — The word valence comes from the French word "avalent" meaning, descending or hanging down, drapery hanging round the bed or the window, tentacles with which things could be caught and kept bound together.

Conception. — On examining the formulae of

(1) the bases.



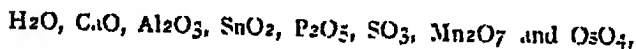
or

(2) the hydrides.



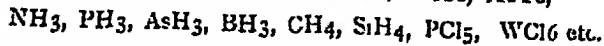
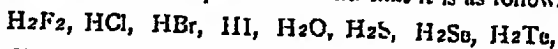
or

(3) the oxides.



or

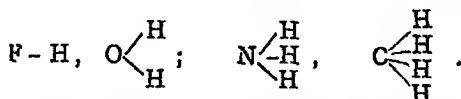
also looking at the molecular composition of even many gaseous or gasifiable binary compounds we find that it is as follows —



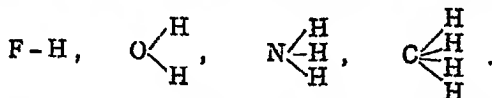
From the above formulae we find that each element (atom) has a peculiar property of combining with a definite number of other elements (atoms). From this it is possible to form a conception of the combining power otherwise called 'Valency' (varying combining powers) of the elements.

Definition : Valency or Valence is that property of an element which expresses the largest number of either atoms with which the atom of a given element is known directly to combine or which determines how many atoms of another kind it can hold in combination.

From the review of the above formulæ we can see that there are different valencies possessed by different elements and for convenience we must have a standard for measuring the same. No binary compound in which one atom of hydrogen combines directly with more than one atom of another element is known.

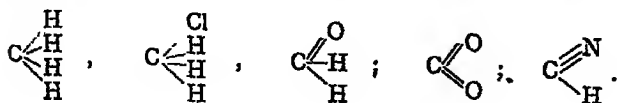


Standard of Valency Hydrogen valency hence is taken as the standard valency, *i. e.* hydrogen is considered as univalent or monovalent. The rest are determined according to this basis and are called di-, tri-, tetra-, and so on *e. g.*



Monovalent	Divalent	Trivalent	Tetravalent
or	or	or	or
Univalent	Bivalent	Tervalent	Quadrivalent
or	or	or	or
Monad.	Dyad.	Triad.	Tetrad.

Further more it has been found that similar relationships are to be found in the compounds which non-metallic elements form with elements other than hydrogen. Thus for example —



Connotation of the word 'Valency.' Here it must be quite clearly understood that we are not at all dealing with intensity of attraction between the elements. It is not a measure of the amount of force but only a measure of the capacity in number.

Hence valency is distinct from combining force or affinity.

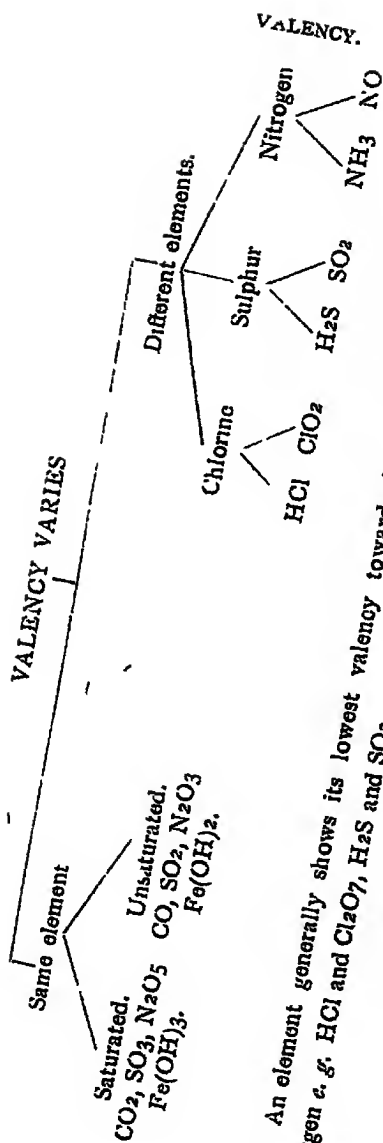
From the above and many other similar facts the conclusion was drawn, that the valency of an element, is a constant property. But it was soon found out that the view could not be maintained without modification.

The existence of gas molecules of HF , HCl , HBr , HI etc shows that the elements F , Cl , Br and I , behave as monovalent and accordingly may be employed as standards in the determination of valency. But this would lead to the conception of a higher halogen valency PF_5 , PCl_5 , Cl_2O_7 .

Upholders of the theory of the constant valency imagined the so called molecular compounds FCl_5 — $\text{PCl}_3\cdot\text{Cl}_2$. But PCl_5 dissolves as such in water and phosphorus fluoride PF_5 is gaseous at ordinary temperature and has undoubtedly the molecular formula PF_5 .

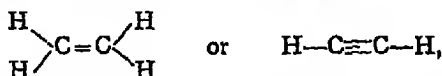
By molecular compounds were meant substances whose structure was inexplicable from the ordinary laws of fixed valency $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, double salts, alums, complex salts, ferro-cyanides, chloro-platinates. It was said that the union of the constituent atoms, in such compounds was of a nature different from that in ordinary compounds. This distinction is unwarranted by facts K_2PtCl_6 , $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$. The difference between the ordinary and the molecular compounds is not intrinsic, but lies only in the fact that the latter is generally more readily dissociated than the former.

Variable Valency From the above it is evident that valency though a constant property is not so rigid as is thought to be, but is variable and changes both with regard to the same element and also sometimes with regard to different elements.



An element generally shows its lowest valency towards hydrogen and its highest towards oxygen e. g. HCl and Cl₂O₇, H₂S and SO₃.

Unsaturated valency. Valency is sometimes so that there is a possibility of multiple bonds like —



as elements appear to display fewer than the normal number of valencies. Thus the formula of carbon monoxide is $\text{C} \equiv \text{O}$, and two valencies of carbon seem to be entirely unoccupied. The same sort of thing is the case with nitric oxide $\text{N} \equiv \text{O}$. That the valencies are really unoccupied and not actively in combination is borne out by the fact that both the compounds readily unite with chlorine, forming carbonyl chloride $\text{Cl} \diagup \text{C} \equiv \text{O}$, and nitrosyl chloride $\text{Cl} - \text{N} \equiv \text{O}$

respectively in which all the valencies are fully employed.

The changes in the valencies confine themselves to narrow limits, and it is very commonly noticed that the changes of valency in the majority of instances take place by pairs of units: *e. g.* by twos (Law of Even numbers) *e. g.*

Sulphur	is	H_2S , (di-)	SO_2 and (tetra)	SO_3 (hexa).
Phosphorus	is		PCl_3 and (tri)	PCl_5 (penta)
Nitrogen	is		NH_3 and (tri)	NH_4Cl (penta)

Here again are to be found notable exceptions *e. g.* NO , ClO_2 , CrCl_2or_3 , FeCl_2or_3 , $\text{WCl}_4\text{or}_5\text{or}_6$ or InCl_2or_3 .

Therefore not only the valencies of the same element vary in different compounds but they not even vary in a regular manner, such as remaining either odd (perissad) or even (artiad).

Although many elements change their valency still at the same time an element almost always shows a characteristic

valency —a valency which remains constant throughout a large and important series of compounds *e. g.*

- (1) Hydrogen and the halogens are monovalent.
- (2) Oxygen and the sulphur group are divalent
- (3) Nitrogen and phosphorus are penta- and tri-valent
- (4) Carbon and silicon are tetravalent.
- (5) The alkali metals are monovalent
- (6) The alkaline earth metals are divalent

This has led chemists to distinguish between Normal or principal, and Contra or supplementary valencies.

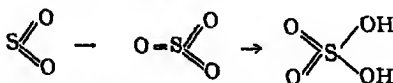
Theory about Valency.

I Abegg's theory Every element possesses a maximum valency of eight made up of positive and negative components or normal and contra valencies Thus —

	SiH ₄		PH ₃		SH ₂		ClH	
	SiO ₂		P ₂ O ₅		SO ₃		Cl ₂ O ₇	
Elements	Na	Mg	Al	Si	P	S	Cl	
Normal	+ 1	+ 2	+ 3	+ 4	- 3	- 2	- 1	
Contra	- 7	- 6	- 5	- 4	+ 5	+ 6	+ 7	

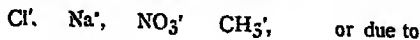
The relative strengths of the two kinds of valency depend upon the chemical nature of the atom itself thus the alkali metals are too electro-positive to show negative valencies fluorine too electro-negative to exhibit positive valencies and thus it cannot combine with oxygen

II Werner's theory The molecules formed by the combination of two or more elements are usually not devoid of the power of combining with further atoms or molecules.



due to the Residual affinity either of the molecule as a whole or of the certain of the atoms contained in them or due to

Principal Valency in the combination of atoms or radicals which can exists as ions or are equivalent to ions



Supplementary valency concerned with the combination of radicals which cannot exist as ions 'OH', 'NH₃', 'ClK', 'CrCl₃'



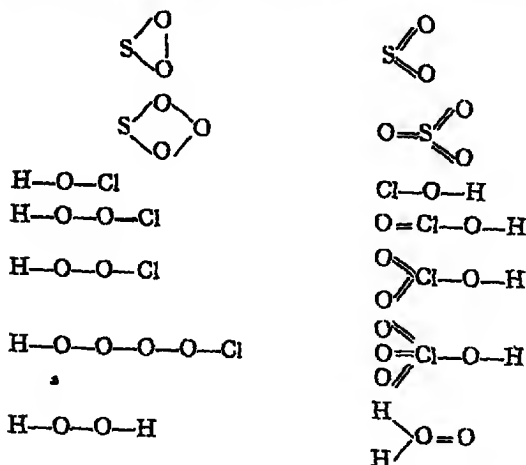
Trivalent cobalt Co can co-ordinate six molecules of ammonia by supplementary valencies Co(NH₃)₆ in which the cobalt atom keeps its principal valencies free [Co(NH₃)₆]Cl₃ to be distinguished from [CoCl₃(NH₃)₃]

Representation of the Valency The usual method to represent a valency is to draw lines between the symbols, the number of lines varying as the valencies do

Each line is to represent one valency. These lines or valencies are sometimes called Bonds or Links

These bonds or links help to depict the graphic or structural formula of a compound.

Determination of the valence In order to ascertain the valency of an atom in a compound—since valency in varying—the constitution i. e. constitutional formula is to be known first, i. e. molecular weight, composition of vapours as well as the chemical behaviour. Thus —



Compounds containing oxygen atoms directly combined together are extremely unstable compounds. But the oxy-acids of chlorine become more stable as the number of oxygen atoms in the molecule increases.

Thus the valency may be determined :

(i) By noting the formula of its compounds with some element of known valency *e. g.* R_2O_3 , $R(OH)_3$, RCl_3 and RH_3 ,

or

(ii) By noting in the formula the number of hydrogen atoms displaced say from sulphuric acid $H_2SO_4 \longrightarrow Na_2SO_4$.

Valency of the Radicals The valency of the radicals is determined by finding out the electrical charges that they are willing to get associated with

Cause of Valence. As to the cause of valency the matter is far from being satisfactorily settled. This much is evident that there is a close connection between the valency of an atom and the electric charge it can acquire under certain circumstances.

Nature of Valency. We have very little knowledge as to why the sodium atom (Na) can hold but one chlorine (Cl) atom, while that of calcium or barium can hold two, and aluminium three each. We really know very little with regard to chemical affinity etc.

Application of Valence. Knowledge of the power of combination -valency- of the different elements helps us a good deal in casting the formulae of their compounds. Thus *e. g.* Na-, Cl-, P≡, Al≡, Sn= or Sn≡ gives NaCl, PCl₃, AlCl₃, SnCl₂ and SnCl₄ etc

The following points are worth noting

(1) Amongst metals, the divalent condition is the commonest.

(2) Some elements have several valencies *e. g.* Sulphur is di-, tetra- and hexa-.

(3) Elements having the same valency or different elements having different valencies variable but belonging to the same numerical order have frequently similar chemical characteristics. e. g. Halogens—Cl, Br, I; Alkali metals—Na, K.—Alkali-earth metals—Ca, Ba, Sr, Mg; Mercurous mercury and cuprous copper— Hg^+ ; Cu^+ ; and mercuric mercury and cupric copper Hg^{++} ; Cu^{++} .

(4) When an element has more than one valency the two (or more) series of compounds are usually totally dissimilar, whilst each series may be very similar to the compounds of other elements of the same valency cf. 3

(5) Elements belonging to the same family have the same valency common

(6) Changes in valency such as take place occur in twos i. e. tri- and penta, di-, tetra and so on [As^{+++} — As^{++} ; Sn^{++} — Sn^{+++}].

CHAPTER XVIII.

Oxidation and Reduction.



The terms 'oxidation' and 'reduction' are two of those few terms with which a beginner in Chemistry gets acquainted, at the very start. But these terms are so peculiar in their character, that the full connotation of these terms is not grasped unless and until the student is fairly advanced, and has grasped the principles of the ionic theory thoroughly. Even the very definition has to be modified twice as the student advances.

The term oxidation, in its narrowest sense, signifies the taking up of oxygen by a substance—an element or a compound—and the substance is said to be oxidised. Thus when copper is heated in air *i. e.* oxygen, it takes up the oxygen and forms copper oxide:



Here copper is oxidised and considering this reaction from the point of view of weight changes, we find that the oxidised copper is increased in weight.:



$$2 \times 63.6 + 16 \times 2 = 2(63.6 + 16).$$

However if hydrogen is passed over heated copper oxide, the latter is again converted into metallic copper, with the simultaneous formation of water:

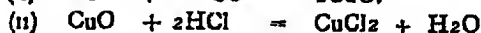


$$63.6 + 16 + 1 \times 2 = 63.6 + 2 + 16.$$

In this reaction the compound of copper has lost the oxygen atom and hence its weight, and to signify this condition

this reaction is termed reduction, and the two terms thus are expressive of reactions that are of opposite character. But these terms have gradually acquired wider meaning. They are now frequently applied to certain reactions in which oxygen takes no part, or also when hydrogen atom or atoms are removed from a compound. Many substances which contain no oxygen have been described as oxidising agents *e. g.* chlorine, bromine, iodine, sulphur etc. Thus when iron burns in sulphur or copper burns in chlorine, the iron or the copper then is said to be oxidised, or even when chlorine liberates iodine from potassium iodide KI, the iodine of the potassium iodide is said to have been oxidised, and these reactions are termed oxidations of iron, copper or iodine.

A simple illustration will clearly show and give some idea of the reasons why the use of the word has been extended. Copper burns in oxygen (cf. the burning of iron wire in oxygen) with the formation of copper oxide a compound with a formula CuO in which copper is divalent. Copper oxide interacts with hydrochloric acid to form water and copper chloride, and in this salt CuCl_2 copper chloride the metal is still divalent.

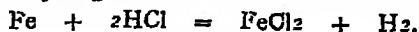


Thus copper is converted into the chloride by the two successive operations of (i) oxidation, and (ii) neutralization, and we find that there is no change of valency in the copper atom after neutralization.

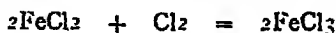
Now copper chloride can be made directly from the metal by burning it in chlorine gas *i. e.* the element can be brought by a single operation, into the same state in which it exists after the two operations of oxidation and neutralization.



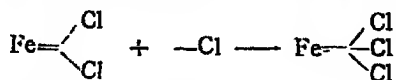
Again iron dissolves in hydrochloric acid and gives ferrous chloride and hydrogen.



Here iron is divalent, but if this very same element is burnt in chlorine it gives iron perchloride FeCl_3 . This ferric chloride FeCl_3 can also be got by the action of chlorine on ferrous chloride.



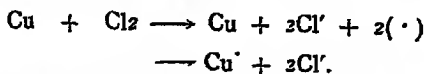
This operation similar to the above is also called oxidation, with chlorine as the oxidising agent, because the valency of iron and the positive charge carried by its ion are increased.



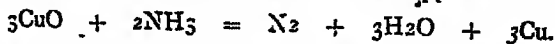
and in terms of ionic hypothesis :—



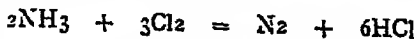
Here it must be clearly borne in mind that it is customary to assume that an element in the free state has a valency of zero. In accordance with this assumption when an element combines with another, say as in the above cases, either with oxygen or chlorine it has to give out its valencies for forming the combination and thus makes the other assume the higher valency : i. e. from zero upwards.



Again to take an instance of a more complicated nature, we find that if ammonia gas is passed over heated copper oxide, nitrogen and water are obtained together with copper.



Here ammonia is said to be oxidised to nitrogen and water. But nitrogen can as well be liberated from ammonia by chlorine.



therefore the action of chlorine over ammonia is called oxidation.

Thus in the light of above instances it follows that the combination of a metal with almost any element (except hydrogen) can be and is regarded as oxidation. Nay even something more has come to be signified. Not merely a combination with oxygen or with any particular element but also an increase in the valency of an element or a radical, and if the compound is an electrolyte a corresponding increase in the electrical charge carried by the ion during the electrolysis has come to mean oxidation.

Combining these ideas we may now say that oxidation is increase in the valency of an element or a radical in the positive direction, or the decrease in the valency of an element or a radical in the negative direction. Since reduction is the exact opposite to oxidation, we may as well say that reduction is the decrease in the valency of an element or a radical in the positive direction or the increase in the valency of an element or a radical in the negative direction.

Electro-negative elements are oxygen, sulphur and the halogens. All acid radicals *e.g.* NO_3' , SO_4'' etc. are electro-negative, while hydrogen and the metals are electro-positive.

Since oxidation involves an increase in the electro-positive charges of an element or a radical, the substances that bring about oxidation : *e.* an 'oxidising agent, must under favourable conditions give out positive charges. Similarly a 'reducing agent' is one which under favourable conditions gives out negative charges.

It should be observed that every reaction that involves change of valency is both an oxidation and reduction. Just as a commercial transaction can be regarded as either a purchase or a sale according to the point of view, so an oxidation process which is always accompanied by a corresponding reduction process may be either called an

oxidation or reduction depending upon the stand one takes. Thus for example, the action of stannous chloride on

(i) mercuric chloride



or, (ii) on ferric chloride

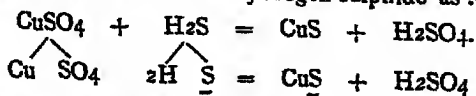


may be either of reduction or oxidation. When stannous chloride is getting oxidised, simultaneously mercuric chloride and ferric chloride are getting reduced. In short oxidation and reduction are invariable concomitants *i.e.* as a rule always occur simultaneously.

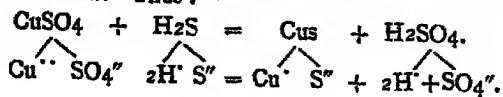
The above cases are cases of double decomposition, and it may be thought by analogy that all double decompositions may be reactions more or less of the above types. Nay it must be always borne in mind that neutralization of an acid by a base, or by a basic oxide does not involve any change of valency, and therefore it is neither an oxidation nor a reduction process, and this is true of double decomposition in general. For example when hydrogen sulphide is brought in contact with copper sulphate solution, copper sulphide and sulphuric acid are formed as .—



Although the percentage of the metal in the copper compound has been increased, oxygen is not abstracted from the sulphate radical and consequently the reaction cannot be called a reduction. The sulphur that is uniting with copper at the second stage *i.e.* of the sulphide, comes not from the sulphate radical but from the hydrogen sulphide as :—

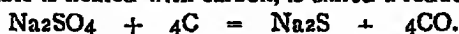


This reaction can be better understood if we study it from the ionic point of view. Thus :—



From the above equation it is evident that in the formation of copper sulphide there is no change in the valency of any of the reacting radicals, and hence simple double decomposition is neither an oxidation nor a reduction process.

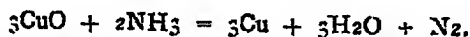
On the other hand the reaction that takes place when sodium sulphate is heated with carbon, is called a reduction,



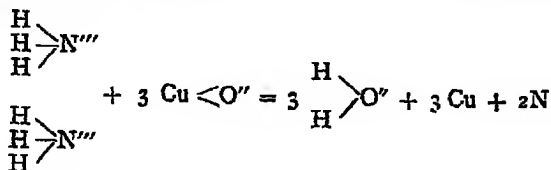
In this equation if we study the different parts, we find that the valency of sulphur which was 'positive six' + 6 () has become 'negative two' -2 (-) i. e. it has been reduced by eight and the elementary carbon atoms have assumed two positive valencies atleast, and thus the sulphur or better the sulphate radical is reduced to the sulphide radical and the carbon is oxidised. Thus sodium sulphate is said to be reduced when heated with carbon the reducing agent which gets oxidised

In the light of what we have gone through so far, let us consider a few of the most important 'oxidation reduction' reactions :—

(1) By passing ammonia over heated copper oxide, nitrogen and water are obtained together with metallic copper
As —

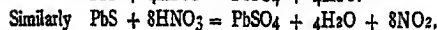
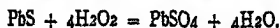


Here ammonia is said to be oxidised to nitrogen and water, because in this reaction if we observe the relative valencies of the different elements in the compounds we find that the nitrogen having a negative valency of three in ammonia, is converted into free nitrogen having no valence. Further copper which has a positive valence of two in copper oxide, becomes zero-valent when converted into free copper. Thus

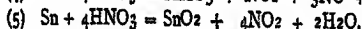
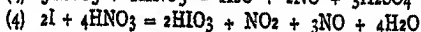
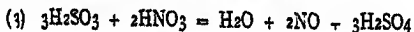


Here ammonia NH_3 is said to be oxidised, and copper oxide CuO is said to be reduced. Similarly nitrogen can be liberated from ammonia by chlorine gas, therefore this action of chlorine on ammonia is also called oxidation.

(2) Again it is very often noticed that oil paintings can be restored to the original shade often by a wash of hydrogen peroxide. The reaction that takes place is as follows :—



In these reactions by noting the change of valency of sulphur which is two negative in the sulphide, and becomes six positive in the sulphate condition, we can see that there is not only a change from negative to positive but a large increase of positive too, hence lead sulphide is oxidised to lead sulphate and hydrogen peroxide or nitric acid is reduced.



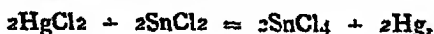
In the above equations (3, 4, 5) we can see by noting the change of valence of sulphur, iodine and tin, that sulphur, iodine and tin are oxidised whereas nitric acid is reduced

Oxidation and Reduction purely from the point of view of Ionic Hypothesis.

Oxidation and reduction here may be reconsidered more in detail in terms of the ionic hypothesis. Thus when a ferrous salt is oxidised to a ferric salt an increase in the valency of the ion takes place. The divalent ferrous Fe^{++} -ion becomes the trivalent ferric Fe^{+++} -ion and since we already know that the individual ions of even one and the same element have specific properties, so in this case the green ferrous ion is transformed into the yellow ferric ion. In the same way the change from the blue cupric ion Cu^{++} to the colourless cuprous

ion Cu may be readily understood. Then again the change in colour when a purple potassium permanganate, KMnO_4 , solution is reduced to an almost colourless solution of a manganous salt, is due to the disappearance of the permanganate ion. So also is the reduction of the yellow chromate or red dichromate to a green chromium salt, caused by the withdrawal of the chromate and the dichromate ions from the solution, and their eventual replacement by the green chromic ions.

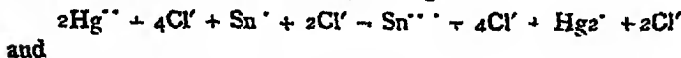
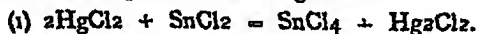
Thus oxidising agents such as nitric acid, chlorine, bromine, permanganates, chromates and ferric salts are substances which produce ions capable of losing part of their electric charges, and of passing them on to other ions which can receive them, and conversely reducing agents in general produce ions which can receive such charges. An excellent example is afforded by the reaction between stannous chloride and mercuric chloride. Thus.



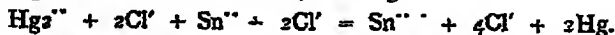
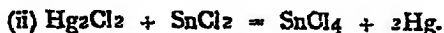
or



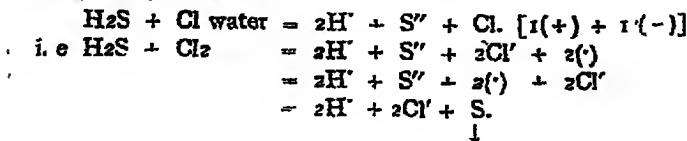
which takes place in two stages as -



and

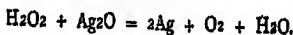


In this example the stannous chloride which provides the stannous ion Sn^{++} is the reducing agent, because the divalent Sn^{++} -ion acquires more charges and becomes tetravalent Sn^{++} -ion. Similarly is the interaction between chlorine water and hydrogen sulphide solution :

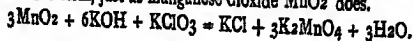


The terms 'oxidising agent' and 'reducing agent' are not only reciprocal to each other, but often are to some extent relative. Thus nitrous acid HNO_2 acts as an oxidising agent towards hydrogen iodide, but as a reducing agent towards potassium permanganate. The same is the case with hydrogen peroxide.

Similarly there are quite a number of substances that behave both as oxidising or as reducing agents, depending upon the conditions under which they are placed. Thus there are often oxidising agents containing oxygen, some or all of which, they can give up to effect oxidation and reducing agents which either do not contain oxygen, and are ready to combine with it or are already containing some and ready still to combine with more. Here one thing that has to be especially marked is the final condition of the substance. If it be carefully observed there are a good many who do act as reducing agents when their usual nature is otherwise. Still they do not get oxidised as one would expect from the reciprocal nature of these reactions: Thus for example hydrogen peroxide:

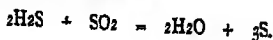


Yet in some cases a substance acts as an oxidising agent and in other cases acts as a reducing agent in the full proper sense of the term, just as manganese dioxide MnO_2 does.



Similarly we find that reducing agents act as oxidising agents, and some reducing agents when they act as oxidising agents get themselves oxidised instead of being reduced.

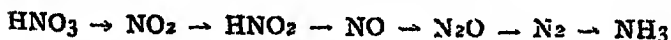
On the other hand some of the reducing agents when they act as oxidising agents, act as oxidising agents in the full proper sense of the term. *e. g.* SO_2 gas



By heating with a nitrate in the dry state, carbon and many other elements can be oxidised :



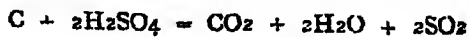
The oxidising action of nitric acid depends upon the reduction of nitrogen. The extent of the reduction depends upon the concentration of the nitric acid and the nature of the substance oxidised. The more concentrated the nitric acid, the less it is reduced. The more concentrated the reducing agent and stronger its reducing power, the greater the reduction of the nitric acid. Nitric oxide 'NO' is commonly formed, but the other products such as nitrogen peroxide 'NO₂', nitrous oxide 'N₂O', nitrogen 'N₂' and even ammonia 'NH₃' are produced. The different stages may well be understood by the following gradations of reduction of nitric acid :



(4) Concentrated sulphuric acid Sulphuric acid decomposes as

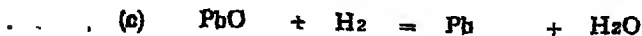
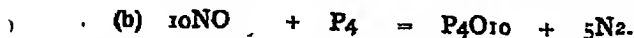
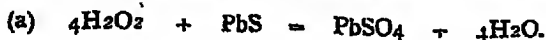


and thus oxidises substances like carbon and iodine :



(5) All peroxides and even many lower oxides

The peroxides and lower oxides being of rather an unstable character give out oxygen easily, and act as oxidising agents as:



(6) Higher oxyacids and their salts.*

The higher acids as well as their salts often times though stable compounds do decompose and liberate oxygen which can be eventually utilized for the oxidation purposes :—

- (a) Potassium chlorate oxidises carbon to carbon dioxide.
- (b) Potassium dichromate oxidises hydrochloric acid to chlorine.
- (c) Potassium permanganate oxidises hydrosulphuric acid to sulphur and water.

(7) Electricity : Electricity is a very important agent in the oxidation reactions. Every change during electrolysis that occurs at the anode (positive pole) is an oxidation in as much as at the anode the negative ion loses its negative charge. The liberation of chlorine or the formation of potassium chlorate by electrolysis is a good example of the

* In the case of the higher oxyacids, salts like potassium permanganate or the dichromate, acid condition chiefly facilitates the oxidation, nay it is in some cases essential. This can be easily seen if a little attention is given to the formation of these salts or better these acids. In the preparation of the permanganates or the chromates a basic compound like potassium hydroxide or carbonate is essential. Manganese and chromium both elements have acid and base forming oxides. Their natural compounds are the lower oxides which have to be changed to the higher ones *i. e.* acid forming ones, by these compounds absorbing oxygen but this is done only through the influence of the base present in the reaction on the principle similar to that of an amphoteric reaction.



Where to change the nature (acid or base) of a compound another compound of opposite nature is to be introduced.

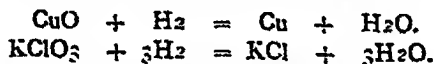
Now if these excess quantities of oxygen are to be withdrawn from this compound from the above reversible reaction, it is evident that an acid is essential for the liberation of oxygen from these compounds.

oxidising action of electricity. It is largely used for obtaining higher oxy-salts and many organic compounds

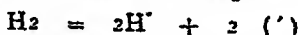
II. Reducing agents

The instances given above as examples of oxidising reactions illustrate as well the reducing properties of the very many substances oxidised, since the properties of an oxidising agent must be exhibited by its interaction with a reducing substance. The most important reducing agents are hydrogen, carbon, carbon monoxide, metals, hydrogen sulphide, sulphur dioxide, heat and electricity.

(1) **Hydrogen** : Hydrogen abstracts oxygen from many oxides and when it is in the nascent state it is strong enough to abstract it from the oxy-acids or their salts :



The reducing action here depends upon conversion of neutral hydrogen into positively charged cations :



(2) **Carbon** : Carbon is the most important reducing agent industrially. In the form of coke or charcoal it is used for extracting zinc, tin, iron, lead and many other metals from their oxides



The reducing action depends upon the readiness with which the neutral carbon atom is converted into an atom with higher positive charges. Hydrocarbons are reducing agents but are seldom employed for this purpose

(3) **Carbon monoxide** Most metallic oxides that are reduced by hydrogen can also be reduced by carbon monoxide :



The reducing action of carbon monoxide here depends upon the conversion of the divalent carbon atom into the tetravalent carbon atom. This is readily seen from the above

reaction taking place in the "Blast-furnace" wherein iron oxide is reduced to metallic iron by carbon monoxide formed from coke and lime-stone.

(4) **Metals.** Metals especially those that have like aluminium and magnesium a great affinity for oxygen and have relatively high boiling points behave as good reducing agents.

(a) Magnesium reduces silica at bright red heat.

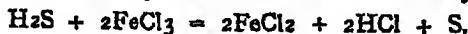


(b) Aluminium as is seen is now quite commonly used in 'aluminothermy' or the 'thermite process'.

(c) The non-metallic elements that unite with oxygen eagerly like phosphorus or sulphur can also act as reducing agents.

The reducing action of the metals depends upon the conversion of the neutral metal into positively charged bodies.

(5) **Hydro-sulphuric acid.** Hydrosulphuric acid is frequently used for effecting reduction in aqueous solutions, and the reducing action depends upon the conversion of the negatively charged sulphur atom into free elementary sulphur.



(6) **Sulphur dioxide or its solution:** This solution is another very useful reducer at ordinary temperatures. As compared with hydrogen sulphide it has the advantage that no sulphur is precipitated during the reduction, but on the contrary sulphuric acid is formed, wherein the tetravalent sulphur is changed to hexavalent sulphur.



(7) **Electricity.** Electricity is a reducing agent too, as every change that occurs at the cathode. (negative pole) during the electrolysis is a reduction, since at the cathode, cation loses its positive charge.

(8) Heat. Heat effects the decomposition of many oxides and oxy-salts *e. g.* KClO_3 . From the point of view of the residue such a change is reduction.

To distinguish oxidising and reducing agents.

In order to find out whether the given substance is an oxidising agent or a reducing agent, its solubility in water should be first tested, and then treated with reagents as follows :—

Reducing Agents.

Soluble.

These are recognised by:—

- (1) The evolution of red brown fumes of NO_2 from HNO_3 .
- (2) Removal of the smell and colour if any, from chlorine water.
- (3) Decolorization of a solution of potassium permanganate acidified with dilute sulphuric acid.
- (4) The conversion in acid solution of orange dichromate to solutions of green chromic salts.
- (5) The decolorization of ferric salts.
- (6) The precipitation of red cuprous oxide from Fehling's solution.
- (7) A production of blue precipitate from a mixture of potassium ferri-cyanide and ferric chloride.

Insoluble.

These are recognised by—

- (1) Combustion in air.
- (2) The liberation of metallic copper or lead from copper or lead oxide on heating.
- (3) The deflagration on heating with powdered alkali KNO_3 .
- (4) The evolution of red brown fumes of NO_2 when heated with moderately concentrated nitric acid.

Oxidising Agents.

Soluble.

These are recognised by :—

- (1) The liberation of chlorine when heated with concentrated hydrochloric acid
- (2) The separation of sulphur from hydrogen sulphide.
- (3) The liberation of iodine from potassium iodide
- (4) The disappearance of the smell of sulphur dioxide
- (5) Conversion of sulphides to sulphates
- (6) The conversion of ferrous salts into ferric salts, tested with potassium ferrocyanide

Insoluble.

These are recognised by :—

- (1) The formation of water when heated in a current of hydrogen or coal-gas.
- (2) The evolution of carbon dioxide when heated with powdered charcoal
- (3) The evolution of chlorine gas from concentrated hydrochloric acid.

N. B.—When the substances are insoluble they should be heated in the solid state, in a suitable gas or with powdered oxidising or reducing agents when both are insoluble.

CHAPTER XIX.

— 0. —

Molecular Weight.

Molecular weight is the weight of the smallest amount of an element or a compound capable of individual existence and the object before us in the present chapter is to find out this smallest weight with individual existence. The question is: How to do it? We have seen that it is possible to calculate the simplest formulæ called the Empirical formulæ—from the results of the chemical analyses—which correctly represent the composition of compounds. But the formula so derived is the simplest possible one and does not represent the exact true composition of the molecule; *i. e.* it does not give us the actual number of atoms of each kind that go to form the molecule of the compound, but gives us only the ratio in which the atoms combine. Thus the simplest formula—Empirical—for hydrogen peroxide (H_2O_2) could be 'HO' but we have reasons for writing it as H_2O_2 . Similarly for nitrogen peroxide NO_2 and hydrofluoric acid H_2F_2 .

Now we can fix on the formulæ H_2O_2 or N_2O_4 or H_2F_2 only if we can get the true weight directly or indirectly of these molecules. If we get the weight of the molecule then we can, from this, easily find the different number of atoms that go to form the exact mass of the molecule.

But can we get the exact weight of the molecule? No. We cannot really get the exact weight of the molecule, because it is a unit which we have only in our imagination and we cannot really handle it so that we can find out its exact weight. But we can get the weight indirectly from the fact that certain properties of substances called the 'colligative properties,' depend on merely the number of molecules present, quite irrespective of their character.

This above fact about the colligative properties makes us have the same properties for the same number of molecules, and provides us a ready means for deciding whether we are dealing with the same number of molecules of different substances and consequently for determining their relative weights. From this and similar other relations we will now try to find out the comparative molecular weights with respect to a standard weight, firstly of gases. The gases presented a great difficulty in the beginning which was settled thus :—

Behaviour of Gases. If different gases are studied with reference to their purely physical properties, we have already seen that all gases expand at the same rate when heated and all gases are equally compressible. There is no difference in this respect between elementary gases like oxygen or hydrogen and compound gases like carbon dioxide or ammonia. Not only this but even active gases like chlorine or hydrogen or oxygen behave exactly similar to nitrogen the most inactive, as compared to these. Hence it is highly unlikely that the elementary and compound gases are differently constituted. From this a law has been established and it is as follows :

“Volume of a gas is proportional to the number of molecules it contains.”

This above statement becomes clear if it is remembered that the pressure of a gas is due to the impact or collisions of the particles of the gaseous body on the sides of the containing vessel, and these impacts are due to the constant motion of the particles, kinetic-energy, of the gas, the speed of which increases or decreases according to the heat applied to the body.

Historically this law was found out by accident, when Humbolt, a naturalist, went to Gay Lussac for the determination of the composition of air from different localities. During these experiments Gay Lussac came upon the regularity of combining volumes and volumes formed when gases combined and formed gaseous compounds. From these

results he came to the conclusion that "When two gases combine, there is an integer ratio between their volumes, as well as between the volumes of either of them and that of the product, provided it is a gas."

From this, as already seen under the discussion of the gas laws, we come to the following facts:—

- 1 vol. of hydrogen + 1 vol. of chlorine = 2 vols. of hydrochloric acid gas
 2 vols " " + " " oxygen = 2 vols. of water vapours.
 3 " " " + " " nitrogen = 2 vols. of ammonia gas
 2 " of carbon-monoxide + 1 vol. of oxygen = 2 vols. of carbon dioxide.

Avogadro's Hypothesis.

Gay Lussac was not slow to perceive that his discovery must have an important bearing on Dalton's "Atomic - Hypothesis." Combining his own experience and the atomic hypothesis together, he came to the conclusion that if elements when in gaseous state, unite in simple proportions by volume, and also in simple proportions by atoms it follows that the number of atoms in equal volumes of different gaseous elements must likewise be simply related.

On this assumption Gay Lussac chose to assume that equal volumes of different gases (at the same temperature and pressure) must contain equal number of atoms. This hypothesis is quite incompatible with the facts observed and leads to inconsistencies.

Because if we suppose that equal volumes contain equal atoms, say '*m*' atoms then according to the observed facts:—

2 vols of hydrogen + 1 vol of oxygen = 2 vols. of steam
 we find that -

$$2 m \text{ atoms} + 1 m \text{ atoms} = 2 m \text{ atoms}$$

i. e

$$2 \text{ atoms} + 1 \text{ atom} = 2 \text{ atoms.}$$

Now when steam is formed it is evident that every particle of steam and according to the above equation every atom of steam must be composed of some hydrogen and some oxygen, but since there can not be less than 1 atom of oxygen in every atom of steam, it follows that each atom of oxygen appears to be split into two halves. But this is a direct contradiction of the atomic hypothesis which clearly states that atom is indivisible further more.

Hence, from the above experimental fact, the inference that can be drawn is that either the atomic hypothesis is wrong or Gay Lussac's assumption must be wrong.

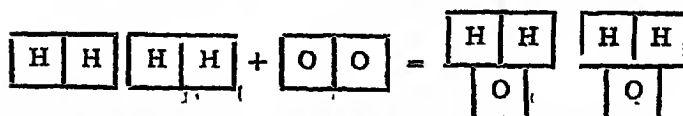
Thus, it became a difficult problem to put the experimental facts and assumption in a consistent fashion so as to be able to agree in all respects. This difficulty, of getting a correct interpretation of the facts and assumptions, was very easily solved by Avogadro. He not only got over the difficulty as said but actually cleared up all doubts and gave a simple and consistent explanation.

Avogadro's suggestion is a very simple one though it introduces important changes. He merely changed the word 'atom' into the word "molecule" because Avogadro assumed the existence of two different kinds of classes of particles :

(1) The physical units composing gases present in equal numbers in equal volumes. These he called "molecules," which really means a small or a tiny collection or a mass of particles.

(2) These molecules in their turn are built up of Dalton's elementary atoms, of the same sort in the cases of gaseous elements and of different kinds in compounds. Thus :

hydrogen		oxygen		steam.
2 vols.	+	1 vol.	=	2 vols.
2 <i>m</i> molecules	+	<i>m</i> molecules	=	2 <i>m</i> molecules.
2 mols.	+	1 mols.	=	2 mols.



$$2 \times 2 = 4 \text{ atoms} + 2 \times 1 = 2 \text{ atoms} = 3 \times 2 = 6 \text{ atoms.}$$

$$6 \text{ atoms} = 6 \text{ atoms.}$$

From the above it becomes quite clear that the substitution of the word 'molecule' for 'atom' in Dalton's hypothesis clears away all the inconsistencies and provides for the splitting up of the particles into any number of smaller particles. This also explains as to why there should be sometimes contraction in the volume of the products formed because the particles may grow up to any size depending upon circumstances.

Assuming the truth of the hypothesis we have at once, a means of setting apart equal number of molecules of various gases, for they will be contained in any definite volume which we may choose. *e.g.* 1 litre. Because as just proved Avogadro says that "Equal volumes of all gases, or vapours, under the same conditions of temperature and pressure contain an equal number of molecules."

Determination of the weight.

Thus we can clearly see that the ratio between the weights of equal volumes say one litre of each of the various gases will be the same as those between the weights of the several kinds of molecules. From this we can get the comparative weight of the molecule of any gas only with reference to any fixed assumed standard.

This standard we have assumed as hydrogen or now-a-days preferably oxygen

Now from the above law of Avogadro we can arrive at the composition of the molecule of hydrogen by making it combine with as many elements as we can to form gaseous products and observing the various stages in which the hydrogen molecule is found to split up. The largest number of divisions that it undergoes being taken as the number of atoms that go to form the molecule of the gas hydrogen, at least so far as our present day knowledge goes. Thus



From the equation it becomes evident that we get two volumes of hydrogen chloride, and as it is hydrogen chloride and hydrogen chloride only, each particle of the gas must necessarily contain some chlorine and some hydrogen. The least we can assume is one atom and hence the molecule is here composed of two atoms at least

The standard selected for comparing the different atomic weights, is hydrogen (or oxygen), where hydrogen atom is taken to be one. This one may be any thing, but to facilitate matters as we already know all these hypothetical ideas have been given a concrete form, and thus the weight of one atom of hydrogen is measured in C. G. S. system and then is taken as equivalent to one gramme though its actual weight may be far too small than one gramme. Thus the hydrogen molecule being composed of two atoms, will be two standards in weight.

The standard unit of weight being one gramme, hydrogen is compared with reference to this one gram weight, and thus the molecule of hydrogen in gram weight will be two grams.

If we determine the volume which this weight of hydrogen will occupy, then we know from the just proved Avogadro's hypothesis that this will be the volume that will be occupied by all kinds of gases provided each is only one molecule

The volume occupied by two grams of hydrogen is found out by actually weighing a certain volume of the gas and calculating the volume necessary for two grams. This is found to be 22.4 litres at N.T.P. This must be the same volume necessary for every kind of gaseous molecule—gram molecule. Thus :—

The molecular weight of a gas is that weight of it, expressed in grams, which occupies 22.4 litres at 0°C and 760 mm pressure

Another statement of the same fact may be given in the following terms :—“The molecular weight of a gas is double its vapour density referred to hydrogen as unit”

The latter statement becomes clear if we remember that the density of a gas is given in terms of the hydrogen volume. If volumes of different gases are compared with reference to the same volume of hydrogen, then it becomes quite clear that we have to multiply the density by two, because our standard is made up of two atoms which are taken as a unit while comparing the density. It is something like expressing a certain weight of a material in different terms. Thus a certain individual may weigh 12 stones but if the weight is to be expressed in pounds then this unit—stone—is to be multiplied by 14, and then he becomes 168 lbs. In exactly in the same way, molecular weights being referred to a standard half that to which the densities are referred to it, must be expressed by numbers which are twice those representing the densities

Thus we can find the weight of the volume occupied by one molecule of a gas, and from this we can fix the molecular formula of any gaseous compound.

It will be more clear by taking a concrete example

Examples .

(1) 120 c.c. of water vapour weigh 0.056 gram at 180°C and 740 mm. Show by means of these data that the molecular weight of water is 18 grams approximately

This is equivalent to showing that the molecule of water vapour which weighs 18 grams must require 22.4 litres of volume according to Avogadro's law.

(a) Reducing the volume of 120 c. c. to N. T. P. we get.—

$$V = \frac{V. P. 273}{760.t} = \frac{120 \times 740 \times 273}{760 \times 453} = \frac{370 \times 91}{453}.$$

(b) $\frac{370 \times 91}{453}$ c. c. is the volume for 0.056 gram of water vapour.

$$\therefore \frac{22400 \times 576 \times 453}{1000 \times 370 \times 91} = 18 \text{ nearly.}$$

From the resolution of the fraction we find that the weight is nearly 18 grams

(2) What is the molecular weight of a gas, 5600 c. c. of which at standard conditions weigh 5 grams? [20]

(3) 16 grams of oxygen will occupy what volume at 0°C and 760 mm. pressure? [11,200 c. c.]

(4) What is the molecular weight of mercuric chloride, the vapour density of which is 9.354 referred to air? [270.9]

(5) Calculate the equivalent weight of the metal of which 0.18 gm. when dissolved in dil. H_2SO_4 evolve 166.7 c. c. of hydrogen at N. T. P. [12]

(6) What volume of CO_2 will be given out by 5 grms. of marble by the action of hydrochloric acid when the experiment was done at 29°C and 756 mm. pressure? [1232 c. c.]

(7) How much of marble and hydrochloric acid containing 22% of HCl are needed to yield 10 litres of carbon dioxide at 15°C and 760 mm. pressure?

(42.36 grms of marble & 140.42 grams of HCl solution.)

(8) 5647 c. c. of a gas measured over water at 24°C and 754.2 mm pressure weighed 6.254 grams, when deprived of aqueous vapour. Calculate the molecular weight. [28.02]

(9) Calculate the molecular weight of methyl alcohol assuming that the following results were obtained in Victor Meyer's (displacement) method of vapour density determinations —

Weight of methyl alcohol = 0.113 gm.

Volume of air collected at 13°C and 762 mm. pressure —
86.2 c. c. [32]

N. B. From the foregoing discussion it is clear that we can get the molecular weights of different gases practically comparatively easily, however three important points must be carefully noticed.

(i) Molecular weights so deduced are entirely relative. The actual absolute weight in grams is left undetermined.

(ii) Molecular weights are deduced from the Avogadro's hypothesis which naturally applies to gases and to vapours only. We do not know and can not infer anything at all about the molecular conditions of a liquid or a solid, from a study of the gas

(iii) The usual methods for the experimental determination of the quantity known as vapour density $\frac{\text{Wt. of the gas vol. contained}}{\text{Wt. of the hydrogen vol. (equal)}}$ are comparatively rough and hence molecular weights so deduced can only be approximate and must always be controlled and corrected by analytical results which are far more accurate.

Avogadro's law gives us a method of finding out the molecular weights of gases or vapours, but if the substance under consideration cannot be converted either to a gas or to a vapour then the law would not help us to find out its molecular weight. But this is not the only method for such determinations.

The molecular weight can be deduced from either :—

I. Vapour density .

It may be sometimes abnormally too

(a) low or (b) high.

II Vapour pressure .

Its influence on the

(a) Raising of the boiling point.

(b) Lowering of the freezing point.

III. Osmotic pressure.

IV. Chemical methods.

We have already seen the effect of foreign particles on the boiling points and freezing points of pure solvents, so also the laws of Osmotic Pressure tell us that the osmotic pressure depends upon the number of particles *i. e.* molecules dissolved in a solvent as is the case with the boiling point and the freezing point. Similarly we have just in this chapter considered that we can get at the molecular weight from the density of a gas.

The only method that remains somewhat not clearly explained is the chemical one.

Chemical Methods for Determining Molecular Weights.

The chemical method though applicable to all the substances still generally it is very complicated and does not invariably lead to definite conclusions.

The result arrived at by the chemical method is the minimum molecular weight. The molecular weights for acids bases and neutral compounds are determined as follows —

I ACIDS —

(a) Direct titration with a standard alkali

(b) Analysis of a salt.

Silver salt is chosen for the following reasons :-

- (i) Usually a normal salt is formed.
- (ii) Slightly soluble in water
- (iii) Has no water of crystallization
- (iv) Easily decomposed

The ratio of the metal to the salt will be that of the atomic weight of the metal to the molecular weight of the salt

The acid is boiled with excess of ammonia until the liquid is neutral. To the cooled solution silver nitrate is added. The precipitate is carefully washed and dried. A portion is then weighed and ignited and the metallic residue of silver weighed.

$$\text{Hence } \frac{W \times 108 \cdot n}{W} = M$$

n = basicity of the acid

w = weight of silver

W = weight of salt.

The molecular weight of the acid is obtained by deducting n atoms of silver and adding ' n ' atoms of hydrogen

Example :-

(1) 0.3652 gm of silver salt of a monobasic acid gave 0.172 gm of silver. Find the molecular weight of the acid

$$\text{Thus } \frac{0.3652 \times 108}{0.1720} = 229.3$$

$$M = 229.3 - 108 + 1 = 122.3$$

(2) The empirical formula of a monobasic acid is CH_2O . 0.2955 gm silver salt gave on ignition 0.1620 gm silver. Find the correct molecular formula

$$\text{Thus } \frac{0.2955 \times 108}{0.1620} = 196.83$$

$$M = 196.83 - 108 + 1 = 89.93$$

The minimum molecular weight of the acid being 90, the molecular formula comes to $\text{C}_3\text{H}_6\text{O}_3$ because the empirical formula weighs 90

II BASES —

(a) **Titration:** This is done by preparing a crystalline salt and purifying it well. Then the amount of the acid present is titrated by means of a standard alkali.

(b) **Analysis of a platinum chloride:** Most organic bases resemble ammonia in forming platinum chloride sparingly soluble, crystallizing well and containing two molecules of the base.

The base is dissolved in a slight excess of moderately concentrated hydrochloric acid and then platinum chloride is added. The chloroplatinate is precipitated, carefully washed and dried. A portion is then weighed and ignited.

$$\text{Thus } M = \frac{W \times 195}{w}.$$

$$M = \frac{m - 409.9}{2} \quad (409.9 = \text{H}_2\text{PtCl}_6)$$

(2) 0.7010 gm of a mono-acid salt gave 0.2303 gm platinum. Find the molecular weight.

$$\text{Thus } \frac{0.7010 \times 195}{0.2303} = 594.$$

$$M = \frac{594.3 - 409.9}{2} = 92.15.$$

(3) The platinum chloride of an organic base gave on ignition 36.9 per cent of platinum. Find the molecular weight.

$$\text{Thus } m = \frac{W \times 195}{w} = \frac{100 \times 195}{36.9} = 528$$

$$M = \frac{528 - 409.9}{2} = 59$$

III Neutral compounds In these cases derivatives must be prepared and examined for the proportion of the total hydrogen replaceable. Thus

Naphthalene by the action of chlorine forms a substance monochloronaphthalene $\text{C}_{10}\text{H}_7\text{Cl}$.

This compound on being treated with bromine, a liquid hydrocarbon of the empirical formula CH yielded a bromo derivative of empirical formula $\text{C}_6\text{H}_5\text{Br}$.

CHAPTER XX

Atomic Weight.

The hypothesis that matter is built up of small indivisible, indestructible particles, is by no means a new one and it can be traced back to the time of Leucippus (428 B. C.) For more than two thousand years the continuity of matter was energetically debated in the schools of philosophy. At the present day the truth of the atomic theory is no longer a matter of dispute, for it has assumed through Dalton (1804) a concrete scientific value based on quantitative measurements. Dalton does not seem to have troubled himself very much about the philosophical discussions. He simply propounded the atomic theory because the laws of combination by weight and particularly the law of multiple proportions are easily accounted for, if we attribute a fixed unalterable mass to each individual atom of the same kind, and assume that atoms of different kinds, having different masses combine together in a simple way to form compounds.

Again we have already seen that every kind of matter is composed of atoms and that these atoms are the smallest divisible particles of elementary substances. Similarly we have also seen that, these atoms of different elements have got different weights. From a mere chemical analysis the information that most we can get, about these weights is that we can come to the various weights of different elements, that go to form the various compounds; *i. e.* what we can get by analysis is the "combining weight." The combining weight of an element, as has been seen, is the smallest quantity of it which combines with or takes the place of one part by weight of hydrogen or eight parts by weight of oxygen.

From the above definition it follows that the atomic weights are either the same as or are multiples of the combining weights

Just as the atomic weight, as said is either the combining weight or an integer multiple of it, so also is the molecular weight a multiple or the same number. That is in short the weight of the molecule of a substance is equal to the sum of the weights of all the atoms which the molecule in question contains. Thus from the relative molecular weight and the quantitative composition of a compound substance, we might expect to get some information as to the smallest proportions by weight in which various elements enter into the composition of the molecules. In short we might expect to get some information as to the atomic weights of the elements.

The different methods that are followed, individually, do not give any fixed and quite positive atomic weights. But it is fixed to the definite number from circumstantial evidence. The more important methods for fixing the relative values of the atomic weights are six.

Methods for determining atomic weights.

- (1) Volumetric method.
- (2) Pure chemical method.
- (3) Method based on Specific Heat determination: *i. e.* on Dulong and Petit's law.
- (4) Method based on Molecular hypothesis.
- (5) Method based on Isomorphism *i. e.* on the law of Mitscherlich.
- (6) Method based on the Periodic System of elements *i. e.* family or group arrangements.

Before we proceed to the determination of definite atomic weights, the most essential thing is to fix the standard on which the weights are to be based.

For many years there was much hesitation as to the "unit" to be adopted in the determination of the relative weights of the

atoms. Dalton proposed to take the atom of hydrogen, as being the lightest known. Wollaston and Berzelius chose the atom of oxygen. But as some atomic weights were found to be smaller than that of oxygen, Wollaston took as unity the tenth part of the atomic weight of oxygen and made $O = 10$. Berzelius chose the hundredth part as his standard and made $O = 100$, with the result that some elements had atomic weights larger than 1,000.

However Dalton was the first to attempt the determination of the atomic weights and according to him

$$O : N : C : H \quad 7.98 \quad 4.67 \quad 5.985 \quad 1$$

On the assumption of greatest simplicity in the molecular structure and the presence of only one atom of each constituent in many compounds practically he made the atom equal to the equivalent weight.

But when we say that water is composed of oxygen and hydrogen in the proportion by weight of 7.98 : 1, it does not follow that the atomic weights of these elements are in this ratio, but only that the weight of all the hydrogen atoms in a given quantity of water bears this proportion to the total weight of the oxygen atoms combined with them, so that

$$n \text{ H} \quad m \text{ O} \quad - \quad 1 \quad 7.98.$$

where n and m represent whole unknown numbers. The atomic theory only teaches us that a certain number of whole atoms of one substance has combined with a definite number of whole atoms of a second element.

$$n \text{ H} \quad \text{with} \quad m \text{ O}$$

The values of n and m are not known. In other words the atomic weights of elements are not necessarily the same as their equivalent weights, they may also be multiples of them by a whole number z .

$$\text{Atomic wt} = \text{Equivalent wt} \times z$$

where z is generally a small whole number. The solution of the problem therefore depends on the value of the equivalent

weights determined with the greatest possible accuracy, and on the value of n .

Thus coming to the point of selecting a standard it is now customary to take the atomic weight of oxygen as 16.00 as the standard, and not hydrogen equal to 1 as the standard. The atomic weights of the remaining elements then have the values that are given in the atomic tables generally used.

For obvious experimental reasons, compounds whose composition is to be determined with the highest attainable accuracy must be easily formed and not readily decomposed. In the case of great many elements, oxides fulfill these conditions best, and in all such instances the deduction from the Law of Reciprocal proportions, of the ratio in which the element would unite with hydrogen involves an exact knowledge of the ratio in which oxygen and hydrogen combine. For many years this ratio was not known with any great accuracy and even at the present time is not considered as a definite fixed number as it depends upon the accuracy of experiments. The change in the ratio would necessarily bring about recasting of the whole atomic weight table. To avoid this uncertainty it was suggested as already seen that, the atomic weight of oxygen should arbitrarily be assumed to be '16' a value not far from the truth, and the atomic weights of all the other elements, including hydrogen, calculated on this basis.

1 Determination of atomic weights by "Volumetric Methods."

We have already seen that all gases at constant temperature, expand or contract equally (atleast very nearly) as the pressure put upon them is decreased or increased respectively (Boyle's law), and under constant pressure the same rise and fall of temperature produces in all gases approximately the same increase or decrease respectively in the volume (Charles's Law).

From the above identical behaviour of gases it follows therefore that the mechanical constitution of all gaseous sub-

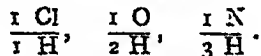
stances must be identical, and in all gases, under the same conditions of temperature and pressure the intra-molecular space is the same, or in other words equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules (Avogadro's Hypothesis).

This is a modification of "Gay Lussac's Law of Gaseous Volumes": Gases combine with one another in simple proportions by volumes and the volume of the gaseous product is simply related to the volumes of the combining gases.

"Now let us suppose that 1 c. c. of hydrogen contains 1000 molecules. Here we do not see why they should combine with chlorine in the ratios

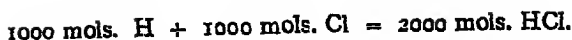
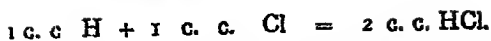
$$\frac{1000}{810}, \quad \frac{1000}{920}, \quad \frac{1000}{1040}, \quad \frac{1000}{1130}, \quad \text{and so on, whilst we}$$

easily conceive such simple ratios as $\frac{1}{1}, \frac{1}{2}, \frac{1}{3}, \frac{1}{4},$ and such simple proportions are experimentally verified.

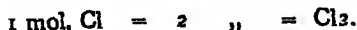


In fact we do not find that 1 c. c. of hydrogen combines with 0.81, 0.92, 1.04, 1.13 c. c. of chlorine but with 1 c. c. exactly. This is easily accounted for if we suppose that 1 c. c. of each gas, under the same external conditions of temperature and pressure, contains exactly the same number of molecules *viz.* 1000 mols.

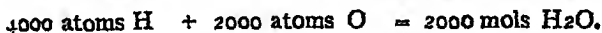
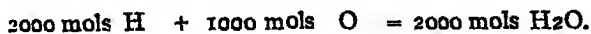
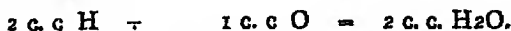
Moreover the particles of all substances in the gaseous state follow laws of combination by volume which are equally definite with those which govern combination by weight. So the proportions by volume of all gaseous bodies which participate in any chemical reaction are in the direct ratio of the number of molecules of each body, or in other words each molecule of a gas represents a unit volume of that body. And since when any two gases are at the same temperature and pressure they contain the same number of molecules in the unit volume," it follows that the volume of any gaseous molecule is the same, at the same temperature and the same pressure. Therefore :—



But each molecule of hydrogen chloride must contain at least one atom of hydrogen and one atom of chlorine since atoms are indivisible :



and applying it to water :



Granting Avogadro's hypothesis, the relative weights of the atoms can be ascertained. A volume of oxygen is found to weigh 16 times as much as the same volume of hydrogen. As equal volumes of these gases contain the same number of molecules, and moreover as the molecule contains two atoms, it follows that an atom of oxygen is 16 times as heavy as an atom of hydrogen

The density of a substance in a gaseous state is a number expressing how many times a given volume of the gas is heavier than the same volume of a standard gas under similar conditions of temperature and pressure. And since in such conditions equal volumes of all gases contain an equal number of molecules, the density expresses how many times the molecule of the substance is heavier than the molecule of a standard gas, in other words, the molecular weights of all gaseous substances are proportional to their relative densities.

We find experimentally that oxygen, marsh gas and water vapour are 16, 8 and 9 times respectively heavier than hydrogen.

Their molecular weights are therefore 16, 8 and 9 times greater than the molecular weight of hydrogen, and as it is understood that the weight of the molecule of hydrogen (H_2) is 2, the molecular weight of oxygen, marsh gas and water vapour shall be

$$\begin{array}{rcl} O_2 & 16 \times 2 & = 32 \\ CH_4 & 8 \times 2 & = 16 \\ H_2O & 9 \times 2 & = 18 \end{array}$$

or the molecular weight is twice the density.

The determination of the approximate value of the molecular weight of the substance, therefore, resolves itself into finding the weight of its vapour in grams which will occupy the same volume as two grams of hydrogen measured under the same conditions of temperature and pressure. This weight is called the "Gram-molecular weight" or "Molar weight" of the substance, and the volume which it occupies is called the "Gram-molecular volume." It is practically the same for all gases and 760 mm and $0^\circ C$ may be taken equal to 22.4 litres

The relationship between the atomic weight of an element and its density in the gaseous state may be expressed as follows:—

$$\text{Atomic weight} = \frac{\text{Molecular weight}}{\text{Atomicity}} = \frac{\text{Density} \times 2}{\text{Atomicity}}.$$

Avogadro's hypothesis (applicable only to gases) gives no direct information concerning the atomic weight even when the vapour density of the element is itself determined. Because we see from the above formula that unless the number of atoms which make up the molecule is known, it is impossible to tell what portion the atomic weight is of the molecular weight.

Under the mistaken impression often repeated by the beginners that the atomic weight of a gaseous element is

always half its molecular weight, some atomic weights can be got as the above statement is certainly the case in some instances yet it is by no means an invariable rule, though at one time it was supposed that the molecular weight was necessarily twice the atomic weight. But we know now that the exceptions are numerous and the relationship often depends upon the temperature at which the density is determined. The molecule of phosphorus vapour is made up of four atoms, and therefore the atomic weight of phosphorus is but a quarter of its molecular weight. On the other hand each molecule of mercury vapour is made up of a single atom, so the molecular and atomic weights are in this case identical. Similarly :

- (1) Arsenic is tetratomic,
- (2) Oxygen as ozone is tri-atomic.
- (3) Helium, Neon, Argon etc. Mercury, Zinc and Cadmium are mono-atomic
- (4) Antimony between 1572° to 1640° is Sb_2 and Sb_3 .
- (5) Bismuth at 1700° is Bi and Bi_2 .
- (6) Iodine and Bromine at high temperature are mono-atomic.
- (7) Sulphur shows a variety as per temperature

In spite of these limitations a great deal may be learnt indirectly from a study of the molecular weights and composition of the compounds of the element whose atomic weight it is desired to be fixed.

Cannizzaro studying the problem of the determination of the number of atoms in a molecule came to the general conclusion —

If the composition and vapour density of a compound of a given element can be experimentally determined, then it is easy to calculate the weight of that element present in the molecule of its compound, relative to that of the hydrogen atom. Since each molecule of the compound must contain a whole number

of atoms of the element in question and this weight must either be its atomic weight or a rational multiple of that weight.

As it is extremely likely that if a sufficient number of compounds of the given element are studied, the molecule atleast of one of them will contain but a single atom of the element, and thus the smallest weight of the element found in the molecule of any of its volatile compounds is most probably the atomic weight sought.

In short for the determination of the (approximate) atomic weight of an element we have therefore two procedures.

- (i) When a single element, then by the formula

$$\text{Atomic weight} = \frac{\text{Density} \times 2}{\text{Atomicity}}.$$

This is useful to fix the true value of the atomic weight only, so far as, the atomicity of the element has been determined.

- (ii) When in a compound condition then.

- (1) Determine the molecular weights of a large number of compounds of the element in question
- (2) Analyse these compounds, and
- (3) Multiply the molecular weight of each by the percentage of the element present in the compound

The least value so obtained will be the approximate atomic weight.

The atomic weight of an element is sometimes defined also as the smallest weight of it (or the Highest Common Factor of its weights) found in the molecular weights of its volatile compounds. Hence the greater the number of volatile compounds examined for the purpose, the greater is the certainty of such a weight being its atomic weight.

As an illustration of the second method, let us suppose the atomic weight of the element phosphorus to be unknown, but the composition and vapour density of a number of volatile compounds of phosphorus to have been experimentally determined.

Thus phosphorus oxide is known to be composed of .

phosphorus = 56.36 % .

oxygen ... = 43.64 %

Its vapour density is 110, and thus its molecule is 220 times as heavy as the hydrogen atom

∴ 100 (phosphorus oxide): 220 :: 56.36 (phosphorus): X

$$\therefore X = \frac{56.36 \times 220}{100} \text{ i. e.}$$

$\frac{124}{220}$ ths of the weight of phosphorus oxide molecules are made up of phosphorus; or in other words the phosphorus oxide molecule contains an amount of phosphorus weighing 124 times as much as the hydrogen atom.

Similar data for a number of phosphorus compounds are tabulated as :—

Compound	per-centage of phosphorus	Vapour density.	Molecular weight	Least weight of phosphorus in the molecule.
1 Phosphorus oxide.	56.36	110	220	$\frac{56.36 \times 220}{100} = 124$
2 Phosphoric oxide	43.66	142	284	$\frac{43.66 \times 284}{100} = 124.$
3 Phosphorus chloride.	22.54	68.75	137.5	$\frac{22.54 \times 137.5}{100} = 31$
4 Phosphorus fluoride	35.22	44	88	$\frac{35.22 \times 88}{100} = 31$
5 Phosphorus penta-fluoride.	24.60	63	126	$\frac{24.60 \times 126}{100} = 31.$
6 Hydrogen phosphide.	91.17	17	34	$\frac{91.17 \times 34}{100} = 31$
Hydrogen phosphide (spontaneously inflammable)	93.94	33	66	$\frac{93.94 \times 66}{100} = 62.$

On inspecting the above table it is at once apparent that the relative weight of phosphorus in a molecule of each of the seven compounds is either 31, 62 or 124 times as great as the weight of hydrogen, i. e. either 31 or a rational multiple of 31.

The weight of phosphorus atom cannot therefore, be greater and in all probability is not less, than 31 times the weight of the hydrogen atom. The probability being all the stronger, the larger the number of phosphorus compounds considered.

Examples

(1) From the data given, deduce the probable atomic weight of oxygen.

Gaseous compound	Relative density	Mol. dens. $\times 28.87$ (approximate mol. wt.)	Molecular weight	Analysis stated in parts by weight of the molecule
(1) Carbon dioxide	1.53	44.2	45.30	31.92 C + 11.37 O
(2) Sulphur dioxide	2.25	64.4	63.92	31.92 S + 31.96 O
(3) Sulphur trioxide	2.40	69.70	79.86	31.92 S + 47.94 O
(4) Carbon monoxide	0.97	27.97	28.93	15.96 C + 11.97 O
(5) Water	0.63	18.2	17.06	15.96 O + 2.00 H
(6) Nitric oxide	1.04	30.0	29.97	15.96 O + 14.01 N

(16 is the atomic weight of oxygen)

(2) Find the most probable atomic weight of carbon from the appended experimental results.

— O: —

Gaseous compound	Relative density air = 1	Analysis in parts by weight.
(1) Marsh gas	0.554	11.97 C + 4.0 H
(2) Methyl iodide	4.883	11.97 C + 126.53 I + 3.0 H.
(3) Chloroform.	4.20	11.97 C + 106.11 Cl + 1.0 H
(4) Carbon monoxide	0.968	11.97 C + 15.96 O
(5) Carbon disulphide	2.645	11.97 C + 63.96 S

(12 is the atomic weight.)

—:O:—

(3) The vapour densities of a number of compounds of phosphorus were determined as follows:—

(1) Phosphoric oxide. P_2O_5	150.
(2) Phosphorous oxide. P_2O_3	110.
(3) Phosphorus trichloride.	70.
(4) Phosphorus penta-fluoride	63.
(5) Phosphorus oxychloride.	77.
(6) Phosphorus pentasulphide.	111.
(7) Tetra phosphorus trisulphide.	114.

Analysis of these compounds gave the following percentages of phosphorus:—

(1) Phosphoric oxide.	43.7 per cent
(2) Phosphorous oxide.	56.4 " "
(3) Phosphorus trichloride	22.5	" "
(4) Phosphorus pentafluoride	24.6	" "
(5) Phosphorus oxychloride	20.2	" "
(6) Phosphorus pentasulphide.	27.9	" "
(7) Tetra phosphorus trisulphide.	56.4	" "

Calculate the probable atomic weight of phosphorus from the above data

[31]

II Determination of atomic weights by "Chemical Methods."

The first step in using this method is exactly the same as for the volumetric method, that is, an analysis is made of the substance, in order to determine the relative amounts of the compounds. The further procedure may be illustrated by reference to water. Water contains in round numbers 1 part by weight of hydrogen to 8 parts by weight of oxygen. If the formula for water is HO , it is clear that the atomic weight of oxygen is eight referred to hydrogen as the unit. If on the other hand, the formula is taken as H_2O , the ratio of the amounts of the two elements to be in agreement with the analysis 1 : 8 ought to be 2 : 16 and therefore the atomic weight of oxygen is 16. Similarly if we take the formula H_3O , the atomic weight of oxygen must be 24, in order to maintain the experimentally found ratio 1 : 8. Now it has been found that hydrogen can be displaced from water in two stages (by means of metallic sodium for instance) and two stages only. As not less than one atom can be displaced at a time, it follows that there are at least two atoms (and probably only two) of hydrogen in the molecule of water. The formula is therefore H_2O and the atomic weight of oxygen is 16. The last conclusion is confirmed by the experimental fact that the oxygen cannot be displaced in stages and therefore only one atom is present.

Further more the cases of methane and ethylene tell us that the ratio of carbon to hydrogen is 1 : 4 and 1 : 2. Methane contains 3 parts of carbon to 1 part of hydrogen (in other words the equivalent of carbon is 3) and ethylene contains 6 parts of carbon to 1 part of hydrogen, and therefore the atomic weight of carbon in this case should be 6. But we know however that one-fourth of hydrogen in methane can be displaced by chlorine, hence methane contains four atoms of hydrogen and to retain the experimental ratio 3 : 1 the atomic weight of carbon must be 12, provided only one atom of carbon is present. The formula for methane is therefore CH_4 , and it can be shown

by similar reasoning that the formula for ethylene is C_2H_4 . The same conclusion can be reached readily by the volumetric method as shown in the case of phosphorus.

Examples .—

(1) If the electrochemical equivalent of oxygen is 7.98, silver is 107.66 chlorine is 35.37, antimony is 39.86 and copper is 31.59, and the hydrogen replacing power of these elements in the compound used in finding the equivalents be for one atom of the element taken : oxygen 2, silver 1; chlorine 1, antimony 2 and copper 2 atoms, what are the atomic weights of these elements ?

$$[O = 15.96, Ag = 107.66, Cl = 35.37, Sb = 119.38 \text{ \& Cu} = 63.18]$$

(2) Dumas found on heating copper oxide in a stream of hydrogen, that a certain weight of this substance lost 59.789 grams of oxygen and yielded 67.282 grams of water. Calculate from these numbers the atomic weight of hydrogen [1.025]

(3) 0.3697 gram of aluminium liberated 0.04106 gram of hydrogen on being dissolved in a strong solution of sodium hydroxide. Find the atomic weight of aluminium, [27]

(4) Stas found after adding 7.25682 grams of potassium chloride to 10.51995 grams of silver dissolved in nitric acid, that 0.0194 gram of silver remained in solution. Calculate from these data the atomic weight of potassium [38.92]

(5) Morignac obtained 314.894 grams of silver nitrate from 200 grams of silver. 14.110 grams of silver nitrate required 6.191 grams of potassium chloride for complete precipitation, and 10.339 grams of silver dissolved in nitric acid required 5.120 grams of ammonium chloride for precipitation. Calculate the atomic weight of nitrogen from these data.

$$\left. \begin{array}{l} \text{[From synthesis of silver nitrate } 13.967 \\ \text{By precipitation with pot-chloride } 14.026 \\ \text{'' '' '' am '' } 13.945 \end{array} \right\} \text{mean} = 13.97.$$

III Determination of the atomic weights by "Specific Heat."

There is another method of determining atomic weights, which has been very serviceable as it is applicable precisely to those cases where the elements form no volatile compounds, and thus where the atomic weights used to be doubtful. Dulong and Petit in 1819 stated that "the product of the atomic weight and the specific heat of solid elements is constant", and this is 6.4 (or 6.25). This product is called 'Atomic Heat', and thus we may state the law of Dulong and Petit thus —

The atomic heats of all solid elements are equal

(Specific heat is that quantity of heat, measured in calories, required to warm 1 gram of the substance through 1°C. The calorie being the quantity of heat required to warm one gram of water through 1°C.)

The specific heats of solid elements are in the inverse ratio of their atomic weights

N. B. [Dulong and Petit's law applies strictly only to solid elements, generally to a metal whose atomic weight exceeds 30].

From the above it is evident that the approximate atomic weight of an element will be given by the equation .—

$$\text{Atomic weight} = \frac{6.4}{\text{Specific heat}}$$

The law is not perfectly accurate as the atomic heats of different elements vary somewhat.

From the above formula we can get the atomic weight, but the quotient is not an exact atomic weight it is only an approximate number, for the law is approximately true

Elements	Specific heat	Atomic weight	Atomic heat = Sp. ht \times at. wt
1 Bismuth	0.0305	206.9	6.3
2. Lead	0.0315	205.35	6.4
3 Gold	0.0317	195.7	6.2
4 Copper	0.0950	63.5	6.0
5 Nickel	0.1084	58.3	6.3
6 Iron	0.1098	55.5	6.1
7 Sulphur	0.1712	31.82	5.4

Examples.

In an experiment it was found that 1.032 grams of tin gave 1.310 grams of stannic oxide on oxidation with nitric acid and subsequent ignition. Given that specific heat of tin is 0.0562. Calculate the atomic weight of the metal.

Inspection of the example tells us here that we will get (1) an approximate atomic weight, (2) also the correct equivalent weight. Thus as Dulong and Petit's law gives us only an approximate value, we must get the equivalent of tin first on which, or its multiple, we can then fix the atomic weight as it is either the equivalent or its multiple. Thus the calculation involves three steps:—

(1) Calculation of the correct equivalent of the metal

$$\begin{array}{rcl}
 1.310 & \text{grams} & \text{Tin oxide} \\
 \hline
 1.032 & \text{,,} & \text{Tin} \\
 0.278 & \text{,,} & \text{Oxygen.}
 \end{array}$$

Thus :—

0.278 grms O. 8 grms. O :: 1.032 grm. Sn : X

∴ The chemical equivalent of tin in the stannic oxide is .—

$$\frac{1.032 \times 8}{0.278} = 29.7.$$

(2) Calculation of the approximate atomic weight from the Dulong and Petit's law

$$\text{Atomic weight} = \frac{6.3}{\text{Sp. Heat}} = \frac{6.3}{0.0502} = 122.$$

(3) Finding of the multiple of the equivalent which is nearest to the approximate atomic weight. [This is the accurate atomic weight].

By inspection the multiple of 29.7 nearest to 122 is seen to be $4 \times 29.7 = 118.8$.

∴ The accurate atomic weight is 118.8.

N. B. Step (3) may be performed in two stages, if the multiple of the equivalent weight nearest to the approximate atomic weight is not (as above) evident at sight, then

(3.a) Find the valency of the metal, thus .—

$$\begin{aligned} \text{Valency of Sn} &= \frac{\text{atomic weight (approx)}}{\text{chemical equivalent}} \\ &= \frac{122}{29.7} = 4 \text{ (to the nearest} \\ &\quad \text{whole number).} \end{aligned}$$

(3.b) Calculate the atomic weight of the metal from its equivalent weight and valency :—

$$\begin{aligned} \text{Atomic weight of Sn} &= \text{Chemical equivalent} \times \text{valency.} \\ &= 29.7 \times 4 \\ &= 118.8. \end{aligned}$$

(2) The specific heat of iron is 0.114 Calculate its approximate atomic weight. (56.1)

(3) 0.5239 gram of a metal of specific heat 0.0936 gave 0.6557 gram of its oxide. Find its exact atomic weight. (63.6)

(4) 1.2169 grams of the chloride of a metal were converted into the sulphate by heating with concentrated sulphuric acid. The weight of the sulphate formed was 1.3270 grms. The specific heat of the metal is 0.0314. Calculate its atomic weight (205.3)

IV Determination of the atomic weights by "Molecular Hypothesis."

Since by hypothesis an atom is indivisible, a molecule of an element or of any of its compounds cannot contain less than one atom of that element.

Hence if we determine the molecular weight of any one compound of a given element, and then by analysis find the weight of the element which is contained in the molecular weight of the compound, it is evident that, the atomic weight of the element cannot be greater than the number thus obtained. We may continue these operations with a large number of other compounds of the same element and the smallest weight of the element which is ever found is evidently the maximum atomic weight.

"The maximum atomic weight of an element is the least weight of it which is ever found in one molecular weight of any of its compounds"

As in the many thousands of carbon compounds, which have been investigated, less than 12 parts by weight of carbon has never been found in the molecular weight of any one, we conclude that the atomic weight of carbon is 12.

V Determination of the atomic weights by

"The Law of Mitscherlich."

There is another very peculiar method, besides those given above, which has been employed for choosing the correct atomic weights, and this is based upon isomorphism. Substances are said to be isomorphous when they show *i.e.* have the same crystalline form and this way of different substances assuming the same form — *i.e.* crystallizing in the same system is isomorphism, and these substances are said to be isomorphous (*isos* = same, *morphe* = form). It may be stated here that, as a general rule isomorphous substances have analogous chemical constitution. Thus if the chemical formula of one substance is known and another substance is found to be isomorphous with it, it may be concluded that, in all probability, the formula of the second substance is analogous to that of the first.

In 1812 Mitscherlich, who had been engaged on the study of the crystalline forms of the salts of phosphoric and arsenic acids with the alkali metals came to the following conclusions —

(i) The form of the crystals of alkali phosphates and arsenates, as shown by the measurement of the angles was the same

(ii) Crystals deposited from a mixed solution had the same form as those deposited from a pure solution of either a phosphate or an arsenate

(iii) A crystal of one of the substances, when placed in the saturated solution of the other, continued to grow by superposition of the second substance, the form of the crystal remaining unaltered

These potassium salts had analogous composition i. e. they contained the same quantity of potassium, oxygen and water of crystallization, and whatever difference was, was only in the weight of the chief element (i. e. phosphorus and arsenic.).

From other similar isomorphous bodies, the chemist generalized the statement that "Substances which have analogous composition crystallize in the same shape. i. e. are isomorphous." Thus when one element replaces another in a compound without altering the crystalline form, it is assumed that they displace each other atom for atom.

A little consideration shows that a method of fixing atomic weights may be based on the above statements. If an element of known atomic weight is displaced by another of unknown atomic weight, the amounts are in the ratio of the atomic weights.

To take a simple example, the two salts potassium chloride KCl and potassium iodide KI are isomorphous, and we assume that the atomic weight of chlorine is known. Analyses show that potassium chloride contains 39 parts of potassium to 35.5 parts of chlorine, and that for the same amount of potassium the other salt contains 127 parts of iodine. Now as iodine is assumed to have displaced chlorine for an atom of it, it follows that 127 is the atomic weight of iodine:

Examples :

(1) Cuprous sulphide and silver sulphide are isomorphous compounds. The percentage of sulphur in the former is 20.14, and in the latter 12.94. Given that the atomic weight of copper is 63.57. Calculate that of silver.

(107.87)

(2) Sodium-hydrogen-arsenate is isomorphous with sodium-hydrogen-phosphate, the latter being represented by the

formula $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ Analysis of the arsenate shows that it contains 18.64 per cent of arsenic. Calculate the atomic weight of arsenic using the following weights:—

$$\text{O} = 16, \text{H} = 1.01, \text{Na} = 23.06. \quad [74.87]$$

(3) The formula for the ordinary potassium alum is $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ Gallium forms a potash alum isomorphous with this and containing 13.52 per cent of the metal. Calculate the atomic weight of gallium. [69.85]

VI Determination of atomic weights from

“The Periodic System.”

When a large number of elements were given their individual atomic weights and also when their chemical and physical properties were studied, especially collectively, it became clear to some chemists that these various elements show a peculiar relationship amongst themselves *i. e.* chemically similar elements possessed either almost the same atomic weights as—

$$\text{Iron} = 55.5, \text{Nickel} = 58.5, \text{Cobalt} = 58.5$$

or else that they exhibited nearly a constant difference like —

$$\text{Chlorine} = 35.2, \text{Bromine} = 79.4, \text{Iodine} = 126$$

i. e. an increase of 44.2 and 46.0 respectively.

The discovery of this general statement about the relationship of the various elements led to the establishment of the Great law called “The Periodic Law of Mendeleeff” which is —

“The whole of the properties of the elements both chemical and physical vary in a periodic fashion with their atomic weights”

He sought to illustrate this law by arranging the elements in a tabular form. This attempt to tabulate the elements gave us the common periodic table. (next page)

THE PERIODIC ARRANGEMENT OF THE ELEMENTS

SERIES	GROUP O	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII
1		H = 1							
2	He = 3.99	Li = 6.94	Cl = 9.1						
3	Ne = 20.2	23 = Na	24.3 = Mg	B = 11	C = 12	N = 14.01	O = 16	F = 19	
4	A = 39.88	K = 39.1	Ca = 40.0	27.1 = Al	28.3 = Si	31.04 = P	32.07 = S	35.46 = Cl	
5		63.6 = Cu	65.4 = Zn	Sc = 44.1	Ti = 48.1	V = 51	Cr = 52	Mn = 54.93	Fe Co Ni 55.9 59 58.7
6	Kr = 82.92	Rb = 85.45	Sr = 87.63	69.9 = Ga	72.5 = Ge	75.5 = As	79.2 = Se	79.92 = Br	
7		107.9 = Ag	112 = Cd	Y = 89	Zr = 90.6	Cb = 93.5	Mo = 96		Ru Rh Pd 100.7 103 106
8	Xe = 130.2	Cs = 132.81	Ba = 137.37	114.8 = In	119 = Sn	120 = Sb	127.5 = Te	126.92 = I	
9				Ce-Yb* 140.25-172					
10									
11		197.2 = Au							Os Ir Pt 191 193 194
12	Nt = 222.4		200 = Hg	204 = Tl	207 = Pb	208 = Bi	U = 238.5		
			Ra = 226.4	Th = 232.4					

* This includes a number of elements whose atomic weights lie between 140 and 173, but which have not been accurately studied, and so their proper arrangement is uncertain

Now if an element is to be given a correct position *i. e.* atomic weight, what one has to do is to expand the properties of the element in question, and the atomic weight may be easily fixed by bringing it to the position which would be conveniently occupied by the element in conformity with its own properties and those that of the neighbours

Reasons for preferring atomic weights to combining weights in representing chemical formulæ.

"There is always a sort of doubt expressed especially by beginners as to why we should have atomic weights as the ruling factors in chemical formulæ, while the elements do not combine according to their atomic weights but do so on the contrary according to their combining weights.

From the foregoing sections the advantages of using the atomic weights in place of the combining weights are evident. Thus if for example we use the combining weight for oxygen 8, the least number of combining weights in a molecule will be 2, and this introduces a needless complication

In the same way, each molecule of a carbon compound would contain 4 or some multiple of 4 as combining weights

Still another advantage of the atomic weights over the combining weights is seen in the Dulong and Petit's law. There is no such connection between the specific heats and the combining weights, as has been shown to hold for specific heats and atomic heats. Finally it is seen that the remarkable relationships between the atomic weights according to the periodic system are entirely absent when the combining weights are used instead "

CHAPTER XXI

— o —

The Law of Mass Action and study of Reversible Reactions.

Every student of chemistry knows that matter is not only indestructible but it (its atoms) also is never at rest and the composing particles are always in a state of constant motion. This though to laymen, appears to be very curious, still it is a fact and best borne out by gases, where the continuous movement of the particles is directly indicated by the pressure they exert. On account of these continuous movements we find that whenever substances having mutual affinity come or are brought in contact with one another, they form compounds, which remain apparently stable or unstable depending upon the force of movement or affinity. The result being the algebraic sum of the two opposing forces. In spite of these things, often times it happens, that on account of the unceasing movements of the atoms, there is a constant tug-of-war between the two forces of affinity and constant motion, leading ultimately to the formation of some particles, and at the very same time to the decomposition of the others, which have been already formed.

The speed of formation or decomposition would be more or less depending upon the possibilities afforded to those varying reactions leading ultimately to a state of equilibrium or a state of affairs where the reaction proceeds with the same speed in both the directions or better where the reaction is reversible.

Reversible reactions are those chemical reactions in which the products of a chemical change, interact to produce the original substances, so that the reaction between the original substances is never complete, no matter how long the process may be carried on. Many of the chemical reactions

are reversible *i. e.* under one set of conditions they proceed in one direction and under another set of conditions they proceed in the opposite direction.

Steam reacts with red hot iron to produce iron oxide and hydrogen .—



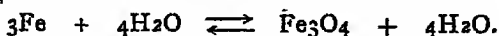
and hydrogen reacts with iron oxide at high temperatures to produce steam and metallic iron .—



Here we are dealing with two independent and antagonistic changes. If, however, iron and steam are heated in a closed vessel so that the products of the reaction are not carried away from the seat of reaction as soon as they are formed, a very curious result is obtained. It seems as if the reaction stops after a time. It is found that 4.58 % of steam remain undecomposed when iron is heated at 200°C in a closed vessel with steam at an initial pressure of one atmosphere.

This means that in a reversible reaction, the two opposite changes take place simultaneously, and set up a state of equilibrium, between the resultants and the reactants of the chemical change. If we start with metallic iron and steam, in the beginning when the reaction is just starting, the velocity with which steam decomposes will be the greatest, because the system then contains the greatest amount of the reacting substance steam. As the concentration of the reacting steam becomes less and less, the velocity of decomposition of steam gradually slows down. On the other hand the velocity of the reaction between H_2 and Fe_3O_4 will be zero at the commencement, because none of the reacting substances are then present. As hydrogen accumulates, the velocity of the reverse change increases. Ultimately a point will be reached when the velocities of the two opposite changes will be equal. One reaction will be balanced by the other and no further chemical change

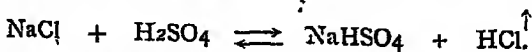
will occur. The reversible reaction is then in a state of equilibrium. For this reason reversible reactions are called opposing or balanced reactions and in order to indicate that the two reactions are proceeding simultaneously from "right to left" and from "left to right," reversed pointers " \rightleftharpoons " are conventionally used in place of the symbol " $=$ ". Accordingly the action of steam on iron is symbolized as follows—



As the constituents of a reversible reaction are in a state of equilibrium, the addition or removal of one of them will cause a disturbance in the equilibrium system. In order to define more clearly the principle governing reversible changes we must introduce the concept of mass action.

Influence of concentration of the reacting substances on the equilibrium

We are now in a position to consider a little more fully, the influence of conditions upon the equilibrium in a chemical system. The first point to be borne in mind is that an equilibrium can only be established when all the reacting substances remain in the system within the sphere of action. If one of the products of the reaction is continuously removed from the system, the back reaction is no longer possible. Suppose we start with sodium chloride and sulphuric acid then we know that if excess of sulphuric acid is used then we reach a certain equilibrium as—



If we heat the substance then we know that the hydrogen chloride being a gas leaves the system being no more soluble at that temperature. The reaction represented by the lower arrow cannot take place and thus the chemical change proceeds practically to completion in the sense of the upper arrow. Here it should be particularly noted that sulphuric acid does not displace hydrochloric acid because the former is stronger than the latter. In fact as we have already seen

hydrochloric acid is stronger than sulphuric acid under equivalent conditions.

Similar is the case in the formation of the precipitates in the reaction of sulphuric acid on, say barium carbonate —



The reaction proceeds to completion in the case of the carbonic acid, as barium sulphate is practically insoluble in water and thus is thrown out of the system in the solid form, in fact as it is produced and thus the product of the reaction is removed and the reaction is not possible.

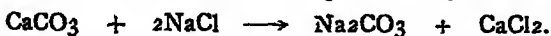
Next comes the point of individual amounts. The first to point out that the chemical change is influenced by the relative amounts of the reacting substances, was Berthollet. He studied the formation of ethyl acetate from ethyl alcohol and acetic acid. In the experiment varying amounts of alcohol were used for one equivalent of acetic acid and the amount of the ester, ethyl acetate formed, was determined by analysis. The following results were obtained —

Amount of alcohol used.	Percentage of ester formed.	Amount of alcohol used.	Percentage of ester formed.
10	100	100	100
20	100	100	100
30	100	100	100

The results show that when one equivalent of alcohol is used, 100% of acetic acid are converted into the ester, whereas if 100 equivalents of alcohol are used 100% of acetic acid are esterified, i.e. the whole amount of the acid is converted into the ester. The results show that the amount of the ester formed and hence the chemical reaction is influenced by the relative

amount of alcohol used. In other words a chemical change is influenced by the relative amounts of the reacting substances.

Besides this example of ester formation many other cases are known which illustrate the effect of mass action. For example, Berthollet noticed large amounts of sodium carbonate (trona) on the banks of salt-lakes in Egypt. He suggested that, the formation of sodium carbonate on the banks is due to the decomposition of calcium carbonate present on the banks of these lakes by sodium chloride brought down by the rivers :



Now the above reaction that takes place on the banks is exactly the reverse of the reaction that usually takes place under ordinary conditions in a laboratory, because calcium carbonate is always precipitated when sodium carbonate and calcium chloride are brought into contact, with each other. Berthollet, however, accounts for the reaction taking place on the Egyptian lakes, as being due to the larger amounts of sodium chloride present, in other words the large amounts of sodium chloride influence the reaction between sodium chloride and calcium carbonate.

The influence of relative amounts of the reacting substances on a chemical action was thus clearly recognised in the times of Berthollet, but was not formulated till Guldberg and Waage (Norwegian investigators) enunciated the law of mass action.

The Law of Mass Action.

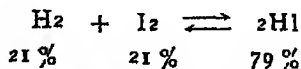
The law of mass action states that the rate of a chemical reaction is proportional to the product of the active mass of each of the molecules reacting and further in a reversible reaction equilibrium is established when the velocities of direct and reverse reactions are equal. The law of mass action can be deduced from a molecular kinetic stand-point as well as from the stand-point of thermodynamics. For the present we shall confine ourselves to the explanation of the terms involved in the law.

First of all the terms "the rate of a chemical action" or "reaction velocity" and "active mass" require some explanation. By reaction velocity we understand the number of gram-molecules of a substance transformed from one system into the other in unit of time (one minute). By active mass is meant not the total amounts of a substance taking part in a reaction, but by the term "active mass" is meant the concentration of the substance in gram-molecules per litre.

It must be borne clearly in mind that the emphasis which is laid at the present time upon the active mass (i.e. the concentration) of reacting substances does not touch the fundamental problem of why the affinity between different substances is so widely different. This merely gives us a mathematical means for experimentally finding out how the influence of mass alters the result of chemical affinity in individual cases.

To come to the law of mass action especially the correct determination on mathematical lines as already said above we must take cases, with systems that remain homogeneous i.e. no precipitate or gas is formed. After choosing such a reaction we have to see the effect of changing the relative amounts of the reacting substances or in short the active mass of the reaction.

Suppose we take equivalent amounts of hydrogen and iodine in a sealed tube and heat it to 445°C we find that after a time equilibrium is established and 79 % of hydriodic acid, HI, are formed and 21 % of hydrogen and iodine remain uncombined.



If now suppose we change the concentration of iodine only, and make it double the first one, it is found out that, instead of 79 per cent, about 93 per cent of the total hydrogen is converted into hydrogen iodide at equilibrium in the above

equation. Exactly the same result is got by increasing the concentration of hydrogen instead of iodine. This can easily be seen from the molecular kinetic stand-point. In the gas there is a constant movement of the molecules of the gases, and for the formation of compounds, the different reacting molecules must collide against one another and the rate of formation of the compound would depend upon the number of collisions per unit time between the colliding molecules.

Thus if in a definite volume of gases the amount of iodine is doubled, the number of collisions per unit time will also be approximately doubled, and the rate of the reaction represented by the upper arrow in our equilibrium reaction is correspondingly increased. This means a different concentration for the equilibrium in the second case to have a balanced reaction. This is only possible if the individual amounts of hydrogen and iodine fall off in the given volume and thus make it possible for a corresponding increase in the amount of hydrogen iodide

Thus it becomes quite clear that the rate of a chemical reaction is proportional to the molecular concentration of each of the reacting substances. At this stage it must be clearly and definitely borne in mind that the rate is not proportional to the total amount of each of the substance present at the time of the reaction, but it entirely depends upon the individual concentration \therefore upon the amount per unit volume. To verify this, let us again take the instance of hydrogen and iodine

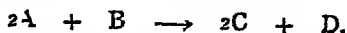
We take two vessels each containing the same amount of iodine while the quantities of hydrogen are taken, say in the ratio 1 : 2. It is evident from what we have already seen that the number of collisions and hence the speed of the reaction in the second vessel will be double that in the first vessel, corresponding to the fact that the concentration of hydrogen is double than that of, in the first. If however, we add more hydrogen as in the case of the second vessel but allow the volume to increase, \therefore the resulting volume is greater than the first one, it

is seen that the speed of the reaction is not doubled. It is clear from the fact that owing to the greater free space which the molecules occupy in the latter case the number of collisions is not doubled by doubling the amount of hydrogen. Thus we see that the rate of change in a chemical reaction is proportional to the molecular concentration of each of the reacting substances. Instead of "molecular concentration" the term "active mass" is preferably used because the latter term may imply that the rate of a chemical change is doubled by doubling the mass of one of the reacting substances, which is not the case unless the total volume is kept constant.

Usually the active mass is represented by enclosing the chemical symbol in a square bracket, *e.g.* $[\text{H}_2\text{O}]$

The second term that requires a little consideration is the employment of the product of the active masses. According to the law of mass action the rate at which A and B are combining, say in the reaction $\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$, is taken to be proportional to the product of active masses of A and B, *i.e.* the rate of combination is equal to a constant $\times [\text{A}][\text{B}]$. The employment of the product of active masses and not any other function (such as sum) is justified by the deduction of the law from the stand-point of thermodynamics

The third and the last point to be considered when applying the law of mass action, is that every reacting molecule must be considered separately because the rate of a reaction is proportional to the product of each of the reacting molecules. Consider a reaction in which 2 moles (molecules) of A, react with 1 mole of B, to form 2 moles of C, and one mole of D. The reaction is:—



In this case the rate at which A and B combine is not proportional to the product of the active masses of A and B, but will be governed by a certain complicated function. In such a case the rate is taken proportional to the '*n*'th power of the active mass of the reacting substance, where *n* is equal to the

number of molecules of the substance taking part in the reaction
In the reaction under consideration, the rate of combination
of A and B is taken equal to

$$= \text{const.} \times [A] [B]$$

These considerations can very conveniently be put in a mathematical form by assuming that two substances, say A and B react to form two new substances C and D as —



Suppose that the respective molecular concentrations at equilibrium are a, b, c and d . Thus the rate of the direct reaction must be in proportion to both a and b , and is therefore proportional to their product. This is represented as —

$$\text{direct rate} = K a b$$

Here K stands for the constant depending upon the mutual affinity between A and B, and the effect of external conditions such as temperature etc.

Similarly,

$$\text{reverse rate} = K' c d$$

At equilibrium the rates of direct and reverse reactions must be equal.

$$\therefore \text{Direct rate} = \text{Reverse rate}$$

$$\therefore K a b = K' c d$$

$$\therefore \frac{a b}{c d} = \frac{K}{K'} = K,$$

where K stands for the ratio of the two constants K' and K , and is also a constant and like K and K' is independent of the concentrations.

This is better seen by supposing that in a certain time t , x molecules of C & D are formed, so that the number of molecules of A and B are reduced to $(a - x)$ and $(b - x)$ respectively.

But the law of mass action states that the reaction velocity is proportional to the active masses present. Hence we have Velocity of the direct reaction (when time ' t ' has elapsed) = $K (a - x) (b - x)$

Finally we come to a point when no further change occurs so that the velocity of the reverse reaction is —

$$K' (x) (x) = K' x^2$$

at equilibrium direct rate = reverse rate

$$\therefore K_1 (a - x) (b - x) = K' x^2$$

$$\text{or } \frac{(a - x)(b - x)}{x^2} = \frac{K'}{K} = K$$

Having considered the terms employed in the law of mass action, let us apply it to a case of reversible reaction. For purposes of application let us select a typical case of a reversible reaction viz. the formation of ethylacetate and water from ethyl alcohol and acetic acid.



According to the law of mass action:

V_1 , the rate of the direct reaction, i.e. the rate of disappearance of alcohol and acetic acid:

$$= k_1 [C_2H_5OH] [CH_3.COOH]$$

Where k_1 is the proportionality factor and the square brackets enclosing the chemical symbols denote the concentrations of substances in gram-molecules per litre at equilibrium.

Similarly V_2 , the rate of reverse reaction, i.e. the rate of disappearance of ethylacetate and water

$$= k_2 [CH_3.COO.C_2H_5] [H_2O]$$

Now at equilibrium the velocities of the two opposing reactions are equal:

$$\therefore V_1 = V_2$$

So also

$$k_1 [C_2H_5OH] [CH_3.COOH] = k_2 [CH_3.COO.C_2H_5] [H_2O]$$

$$\therefore \frac{[CH_3.COO.C_2H_5] [H_2O]}{[C_2H_5OH] [CH_3.COOH]} = \frac{k_1}{k_2} = K$$

where K is called the "equilibrium constant" of the reaction, the value of which only varies with the temperature.

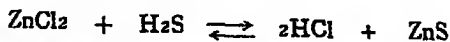
The mathematical relationship deduced above, enables us to investigate the effect of varying the constituents of the

reversible reaction already in equilibrium. Suppose in the above case, we diminish the concentration of water. The value of the numerator will be diminished, for equilibrium, K , has a constant value and under the new change it can retain its constant value if, simultaneously with the numerator, the denominator also decreases. Now the denominator can only decrease if the concentration of alcohol and acetic acid diminishes which can only happen by the formation of ethyl acetate. Hence if we decrease the concentration of water, more of ethyl acetate is formed. Similarly it can be shown that if we increase the concentration of alcohol or acetic acid, more of ethyl acetate is formed.

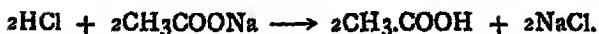
The above result may be stated as follows.—If one of the constituents of a reversible reaction already in equilibrium is removed, equilibrium is destroyed and further change proceeds in the direction where the substance is removed till equilibrium is re-established. On the other hand, if one of the constituents of a reversible reaction is increased, further change proceeds in the direction opposite to that where the substance is added.

These are quite general rules and show qualitatively how the reversible reaction is displaced with changes of concentration. We will now illustrate the application of these rules, by considering a few well known reversible reactions.

When hydrogen sulphide is passed in a solution of zinc chloride, zinc sulphide is formed but only a part of the zinc is precipitated as sulphide. On the other hand, if hydrogen sulphide is passed into a solution of zinc chloride containing excess of sodium acetate, all the zinc is precipitated as sulphide. The usual explanation, apart from the hypothesis of ionization is that, the formation of zinc sulphide from zinc chloride and hydrogen sulphide is reversible :



The presence of sodium acetate decomposes hydrochloric acid by double decomposition, with the formation of acetic acid :—



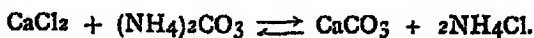
The hydrochloric acid being removed, the change proceeds in the direction where the acid is removed, *i. e.* in the direction represented by the upper arrow with the formation of hydrochloric acid and zinc sulphide. Now if the sodium acetate be present in excess, hydrochloric acid is removed as soon as it is formed, and the change continues proceeding in the direction of the upper arrow, till all the zinc is precipitated.

A still better illustration of a reversible reaction is the formation of bismuth oxychloride from bismuth chloride and water.



If hydrochloric acid is added to the system, the equilibrium is displaced in the direction represented by the lower arrow, and a homogeneous solution is obtained. If on the other hand excess of water is added to the homogeneous solution, the equilibrium is displaced in the direction of the upper arrow and a precipitate of bismuth oxychloride is formed.

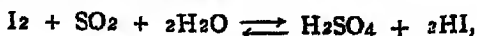
Still another example of a reversible reaction is the formation of calcium carbonate from calcium chloride and ammonium carbonate :



A solution of calcium chloride yields a white precipitate with ammonium carbonate, yet if calcium carbonate is boiled with ammonium chloride in excess, the change proceeds in the direction of the lower arrow with the disappearance of calcium carbonate.

It is important to bear this in mind in analysis, since traces of calcium might be overlooked if great excess of ammonium chloride is present.

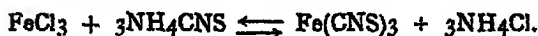
Other examples of reversible reactions are the interaction of iodine, sulphur dioxide and water.:



and the interaction of steam and iron filings which are studied in the manner indicated above.

Experiments.

1. Study the effect of adding ferric chloride, ammonium sulphocyanide and ammonium chloride in the case of the following reversible reactions :—



First prepare the following solutions :—

NH_4CNS sol. . . 3.7 grams of NH_4CNS in 100 c. c. of water.

FeCl_3 sol. . . 3.0 grams of FeCl_3 in 12.5 c. c. of concentrated hydrochloric acid in 100 c. c. of water.

NH_4Cl . . a saturated solution.

Now mix 5 c. c. of ferric chloride and 5 c. c. of ammonium sulphocyanide solutions in a beaker and dilute the solution to two litres with water. Divide the solution between four beakers and place them on a white paper.

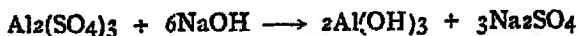
To the second and the third beaker add 5 c. c. of ferric chloride and 5 c. c. of ammonium sulphocyanide respectively, whilst to the fourth beaker add 50 c. c. ammonium chloride solution, and note the colour changes by comparing the tints with the original mixture in the first beaker.

Results .—

5 c. c. of FeCl_3 sol. + 5 c. c. of NH_4CNS sol. when diluted to two litres give a pale red mixture.

Interpretation :—

The white precipitate is due to the formation of aluminium hydroxide :—



The white precipitate is then dissolved in excess of sodium hydroxide with the formation of sodium aluminate, which takes place according to the following reversible reaction :—



or in terms of ionic theory :—



When the concentration of OH' -ions is increased by the addition of excess of NaOH , the equilibrium is displaced in the direction of the upper arrow, and the precipitate dissolves. When, however, ammonium chloride is added, the NH_4' -ions combine with OH' -ions to form undissociated NH_4OH and thus diminish the concentration of OH' -ions. The concentration of OH' -ions being decreased, the equilibrium is displaced in the direction of the lower arrow, with the formation of insoluble aluminium hydroxide

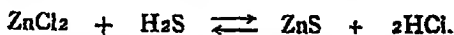
V Investigate the action of hydrogen sulphide on the given zinc chloride solution, alone and in presence of hydrochloric acid and sodium acetate :—

Experiments	Observations
Sol + H_2S in excess	A white ppte
Sol + H_2S and then add HCl	A white ppte which dissolves on the addition of HCl
Sol + HCl in excess, and then add H_2S in excess	No ppte

Experiments	Observations
Sol + HCl in excess + CH ₃ COONa in excess and then add H ₂ S in excess	A white ppte

Interpretation —

The white precipitate is due to the formation of zinc sulphide which takes place according to the following reversible reaction :—



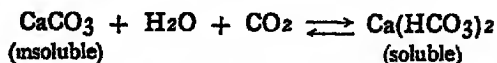
When the concentration of hydrogen sulphide is increased, the equilibrium is displaced in the direction of the upper arrow with the formation of insoluble zinc sulphide. On the other hand when the concentration of hydrochloric acid is increased, the equilibrium is displaced in the direction of the lower arrow and a clear solution results. The sodium acetate combines with hydrochloric acid and forms sodium chloride and undissociated acetic acid, and hence diminishes the concentration of hydrochloric acid which displaces the equilibrium in the direction of the upper arrow with the formation of insoluble zinc sulphide.

VI Investigate the action of carbon dioxide gas on the given milky liquid consisting of calcium carbonate suspended in water.

Experiments	Observations
Pass CO ₂ in the milky liquid for a very long time	The solution becomes clear.
Heat the clear solution obtained above in a test tube	The solution becomes turbid

Interpretation :—

The clear solution is due to the formation of soluble calcium bicarbonate which takes place according to the following reversible reaction :—



When the concentration of carbon dioxide is increased by passing the gas in solution, the equilibrium is displaced in the direction of the upper arrow and a clear solution is obtained. On the other hand, when the concentration of carbon dioxide is decreased, by heating the clear solution so as to expel the dissolved gas, the equilibrium is displaced in the direction of the lower arrow with the formation of insoluble calcium carbonate.

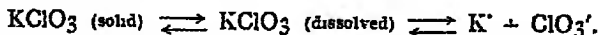
CHAPTER XXII

The Theory of Precipitation.

Solubility Product.

We know from the considerations advanced in previous chapters that when a solid is either thrown out of the solvent or when it does not dissolve it behaves so in obedience to certain laws, especially the law of mass action. This behaviour is of considerable importance from the point of view of Analytical Chemistry. When a substance, say sugar, or common salt, is thrown into water some of the molecules of the solid - salt or sugar - enter into the liquid - water - and in accordance to the kinetic theory move about in all directions in the liquid. These will after a time return to the solid. As more and more solid dissolves more and more number of molecules will be returning to the solid. This will go on until the number of molecules entering the liquid and the number leaving it, in unit of time are equal. When this condition prevails equilibrium is established and the number of the dissolved molecules is a constant.

This solution is then said to be saturated as it can not take in any more of the solute. In a saturated solution of this kind of a salt at a definite temperature there are two equilibria. (1) between undissolved solute and the undissociated molecules in solution, (2) between the non-ionized salt and the ions



Further since the solution is saturated the concentration of the non-ionized salt in the solution must be constant at constant temperature just as sugar has a constant solubility at a definite temperature. Thus the equilibrium between the dissociated and undissociated, and thence between dissolved and

undissolved salt depends upon the product of the concentration of the ions being kept at a certain value. Thus from the law of mass action we have :

$$[K][ClO_3'] = K[KClO_3] = S.$$

$$C_K \times C_{ClO_3'} = K C_{KClO_3} = K$$

As the right hand side of this equation is constant at constant temperature, the product of the concentration of the two ions is also constant at constant temperature. If the concentration of one ion becomes increased or diminished, that of the other must be proportionately diminished or increased, so that the product of these concentrations remains constant or equilibrium will be disturbed and the salt will be precipitated or dissolved.

Precipitation of a salt thus results when the concentration product of the ions of the salt is made to exceed a maximum which is a function of the solubility of the salt in question.

Therefore in a saturated solution of a given ionogen the product of the concentration of its ions is a constant and is called the "Solubility Product." This to put it mathematically is thus. If the concentrations of the two ions are a and b and that of undissociated salt c we have the equation

$$ab = kc$$

(k being a constant for a fixed temperature)

The product ab has a definite value for every saturated solution -since c is definite-. This value is the above named Solubility Product of the substance in question. If in any case the product ab is less than this value no precipitate will come down because the solution is an unsaturated one. But if the product ab is greater than the solubility product, the precipitate is formed.

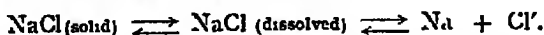
The ion product and therefore the solubility of a substance may be altered in the following five ways by addition of a reagent which

- (1) contains a common ion.
- (2) forms with one of the ions a slightly ionized compound.

- (3) unites with one of the ions to form a complex ion.
- (4) and also by the addition of a strong acid or a strong base to an amphoteric substance or
- (5) alters the charge on one of the ions (oxidation or reduction).

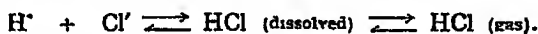
I. Common Ion.

(1) In a solution of sodium chloride when it is saturated we have the following state of equilibrium



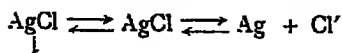
By the introduction of a chloride say hydrogen chloride HCl, the equilibria are disturbed and reversed by the presence of Cl' -ions from the HCl which is highly ionized, when added.

(2) The same might be said also of the preparation of hydrochloric acid gas by the addition of sulphuric acid to a solution of hydrochloric acid.

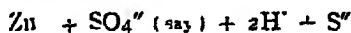


The effect is due to the formation of non-ionized HCl on account of repression of the ionization of the hydrochloric acid

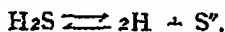
(3) Again if a soluble chloride say NaCl is added to a solution of a silver salt then immediately silver chloride Ag_2Cl_2 is precipitated. The solution gets saturated with respect to silver chloride when $C_{\text{Ag}} \times C_{\text{Cl}'}$ reach the solubility product value K_{AgCl} for silver chloride. Further addition of the chloride increases the ion product above the solubility product value. This disturbs the equilibrium $\text{AgCl} \rightleftharpoons \text{Ag}' + \text{Cl}'$ and reduces the concentration of the silver ions. As the concentration of the silver ions can only be reduced by uniting the chlorine ions to form the non-ionized AgCl, the solution gets supersaturated with respect to AgCl molecules. Some silver chloride must therefore be thrown down to establish the equilibrium



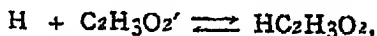
II Slightly ionized compound A given ion may be reduced to nothing when the compound formed is soluble but very slightly ionized This is very nicely illustrated by the formation of the zinc sulphide in the qualitative analysis The sulphide is not completely precipitated if sodium acetate is not added to neutralize the acid set free from the zinc salt When we add hydrogen sulphide solution to a zinc salt solution we have the following ions



The sulphide of zinc will be formed but at the same time a strong acid—in the above case sulphuric acid—would be also resulting and owing to the high H' -ion concentration the S'' -ion concentration from the H_2S added



is reduced to such an extent that no precipitation occurs. By the addition of an excess of sodium acetate the free H' -ions are enabled to combine with the acetate ions and set an equilibrium like this.

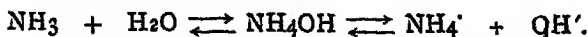


because the acetic acid is a very weak acid and the dissociation is very low This keeps the concentration of the H' -ions too low to have any marked effect upon the concentration of the S'' -ions so that the precipitation continues to completion.

III Hydrolysis These are very common types and can be easily understood by referring to the chapter on hydrolysis.

IV. Complex ion During the analysis of a zinc salt we find that if ammonium hydroxide is used for the precipitation of the hydroxide, we do get a precipitate just in the beginning but on further addition of the reagent the precipitation instead of being more complete, in accordance with the law of mass action, gets dissolved more and more unlike the other precipitations.

What may be the reason? The only explanation is that the zinc radical is combining with some other radical and forming a new product which must be highly soluble, and this can only be accounted for by the behaviour of the precipitating reagent ammonium hydroxide. This is a compound which we know has different radicals in solution. The following is the equilibrium existing in its solution :—

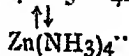
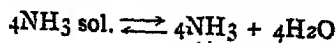
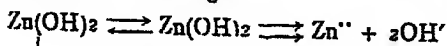


On examination of the newly formed solution of the zinc salt (and similar other salts say of copper, silver etc.) it is found to possess a complex ion $\text{Zn}(\text{NH}_3)_4''$. From the principle of the solubility product

$$C_{\text{Zn}''} \times C_{\text{OH}'} = K$$

it is clear that an increase of OH' -ions above that is necessary to reach the solubility product for $\text{Zn}(\text{OH})_2$ must result in a decrease of the Zn'' -ion concentration. The concentration of Zn'' -ions can be decreased either (1) by the formation of undissociated $\text{Zn}(\text{OH})_2$ and the consequent precipitation of it or (2) by its union with free ammonia to form the complex ion $\text{Zn}(\text{NH}_3)_4''$.

The greater proportion of free ammonia and the slight dissociation of the complex ion $\text{Zn}(\text{NH}_3)_4'$ both influence the equilibrium towards the formation of the complex ion, and therefore we get the following.—



Thus the solubility product is not reached and more $\text{Zn}(\text{OH})_2$ will dissociate and the precipitate will pass into solution

V. **Amphoteric substances (electrolytes).** An amphoteric (amphoterous=both.) electrolyte is one whose hydroxide in solution dissociates both as an acid and as a base, i.e. it

produces both the hydroxyl and hydrogen ions according to the prevailing conditions *e. g.*



Thus the precipitated hydroxide may be made to dissolve by pushing back the dissociation in another direction, and the precipitating reagent itself again dissolves the precipitate. Here though it appears as if a complex radical is formed as .



still looking at the thing from purely ionic point of view, we see that one kind of dissociation is reversed and another kind is given rise to and the substance -hydroxide- behaves as an acid instead of as a base

What really happens in the above case is this

(1) When a strong acid is added the high concentration of H⁺-ions disturbs the equilibrium owing to the union of H⁺ and OH'-ions to form the very slightly ionized water H₂O molecules. Thus non-ionized Al(OH)₃ has to dissociate more to furnish the OH' radicals, with the final result that the hydroxide is dissolved *i. e.* here the hydroxide behaves as a base

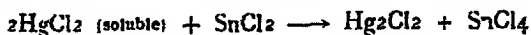
(2) When a strong base is added the high concentration of the OH'-ions disturbs the equilibrium by using up the H⁺-ions present in forming water as above. This makes Al(OH)₃ dissociate further as an acid to give the H⁺-ions required with the result that Al(OH)₃ is dissolved and the hydroxide acts as an acid

This is the case with compounds of zinc, lead, tin and antimony. It must be well noted that a weak base like

ammonium hydrate NH_4OH will not have the same effect owing to the much smaller concentration of OH' -ions

VI Oxidation and Reduction. The meaning of these terms will be clear by referring to the chapter on this subject. But with regard to the solubility product one or two typical examples may serve our purpose sufficiently. Thus :—

(a) A chloride of mercury though soluble is thrown down as a precipitate which is also a chloride of mercury, but on analysis they show to be of different composition. One contains more mercury and the other more of chlorine.



Here the tin reduces the Hg' (mercuric) to Hg_2'' (mercurous) and the values

$$C_{\text{Hg}'} \times C_{\text{Cl}'} = K \quad \text{and}$$

$$C_{\text{Hg}_2''} \times C_{\text{Cl}'} = K$$

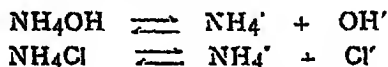
are quite different and hence one is far more soluble than the other. Thus by reduction of mercury we get the solubility affected.

N. B

In analytical chemistry the principle of reaching the solubility product is quite a common occurrence, but sometimes more complicated issues are avoided by keeping back certain elements by not allowing the solubility product of their compounds to be reached. Every student of even simple analytical chemistry knows that the reagent ammonium chloride NH_4Cl serves a very useful purpose.

Hydroxides like those of magnesium, manganese, etc., are not precipitated by ammonium hydroxide when to the original

solution ammonium chloride is already previously added. What happens here is this that the two compounds of ammonium radical dissociate thus



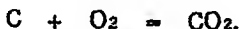
and as there is to be a particular concentration of the NH_4' -ions the already existing NH_4' -ions do not allow the reagent ammonium hydroxide NH_4OH to dissociate to such an extent as to form a sufficient number of OH' -ions from the ammonium hydroxide NH_4OH . Thus as the necessary number of OH' -ions are not formed the solubility product of the hydroxides of the above mentioned metals is not reached, and thus their precipitation is avoided.

CHAPTER XXIII.

Thermo-Chemistry.

It has been already seen that matter is continuously undergoing change though it is indestructible, i. e. it is constantly undergoing action and reaction. These are either spontaneous or otherwise solely depending upon the total energy changes. In every chemical action two changes take place. (1) There is a change of properties of the reacting substances and (2) there is either an absorption or evolution of heat *e. g.* Burning of charcoal.

Chemical changes are invariably associated with energy changes in the system and by means of symbols and formulæ chemists express, in the form of equations a certain amount of information with regard to these chemical changes. Thus the equation

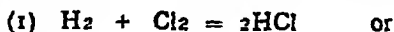


expresses certain number of facts about the quantities of the reacting materials and the quantities of the products formed. All such equations bear upon the face of them the truth that matter can neither be destroyed nor can be created. It very often happens that heat and some other forms of energy are given out as the result of chemical combinations though the total quantity of matter taking part in the reaction is unaltered by the process, although it appears in altered form in the products of the reaction.

In all the chemical changes, besides matter, energy also takes a part and not only do the materials concerned undergo rearrangement or readjustment of energy, but at the same time there is a rearrangement or readjustment of energy as well.

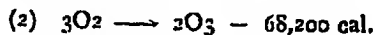
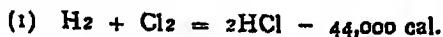
On the basis of the law of the conservation of energy we can see that the free element possesses more chemical energy than the resulting compounds and that the chemical changes are accompanied by a simultaneous transformation of chemical energy to an equivalent quantity of other forms of energy mainly heat. The department of chemistry that deals with the heat equivalent of chemical changes is called thermo-chemistry

The energy changes that take place cannot be judged from the bare equation e.g.



These equations cannot show us that hydrogen and chlorine combine with explosive violence, nor the most violent decomposition of nitrogen trichloride into nitrogen and chlorine

These heat energy changes are represented by using the numbers expressing the heat change, measured in calories with a '+' sign' for evolution of heat, and a '-' sign' for the absorption of heat. Thus



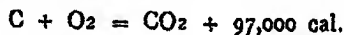
tell us that in the first equation heat is given out, while the second requires heat for transformation to take place

The amount of heat given out or absorbed when a substance is formed is called its heat of formation, and the heat given out or absorbed when a substance is split up is called the heat of decomposition. Most of the substances are formed with evolution of heat. Chemical compounds formed with the evolution of heat are said to be exothermic, whilst substances formed with absorption of heat are called endothermic. It can easily be seen from the above that heat must be supplied to split up exothermic substances,

whereas endothermic substances decompose with evolution of heat. Similarly it is evident that if the other conditions are kept constant, rise of temperature favours the decomposition of exothermic compounds, but favours the formation of endothermic compounds from their components.

Two other terms employed in thermochemical calculations are (1) Heat of combustion, and (2) Heat of solution. The heat of combustion of a substance is the amount of heat given out when one molecule of it is completely burned. This term is usually used with reference to combustion in oxygen. The heat of solution is that amount of heat given out when one molecule of a substance is dissolved in a large excess of the solvent.

Total, free and bound energy. Mere inspection of a thermochemical equation like



can not tell us whether the heat given out was all at once or in periodic instalments, nor we can gather whether that is the only change in the chemical energy or some other transformations have taken place. We have no way of getting at the total chemical energy in an element for we can never be able to examine it when it has lost all its power of combination, and still further nor have we got any theoretical bases for calculating it. All that is possible is to determine the difference in the energy between two different stages of conditions of combustions. The heat of reaction can not lead us to judge the total energy in the reacting substances but only the change in the chemical energy on the reaction taking place. This latter quantity of energy is termed as the free energy and the remaining energy which cannot be measured is called the bound energy. It can be quite easily seen that the latter is very much greater than the former.

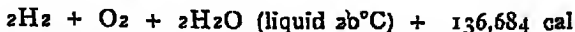
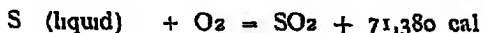
Chemical energy is a relative quantity. Every element is attracted towards every other element with the ultimate result of formation of a compound. But the mutual

attraction is chiefly based upon that peculiar quality we have as affinity for one another.

There is no way for determining it except by measurements. We are not in a position to state what amount of total energy the element, say carbon, possesses except mere statement as to how much it evolves when it combines with hydrogen, or oxygen or with sulphur. As a rule the heat of reaction gives us a clear idea as to the intensity of chemical affinity between different substances but it is not always so. In short heat of reaction is not always proportional to chemical affinity.

Energy Contents of Different Forms of Substances

We know that the different states of matter—solid, liquid and gaseous—are depending upon temperature. Hence it is very important to remember in writing thermochemical equations to see that the particular forms of substances taking part in the reaction are clearly stated as there is bound to be a considerable difference in their energy contents. Not only this but even changes in the state, *i.e.* crystalline form, accompany chemical reactions and these modify to quite an extent the total heat change in the reaction. Thus.



Thus here we can clearly see from the equations that 300 cal represents the heat of fusion of sulphur, and in the last two equations the difference is due to the heat of vaporization *i.e.* change of liquid to the gaseous state.

One more thing that is to be remembered is this, that there is a great amount of change in heat energy if during the reaction gases are formed or disappear as the result of a chemical change. When a gas is generated under atmospheric pressure

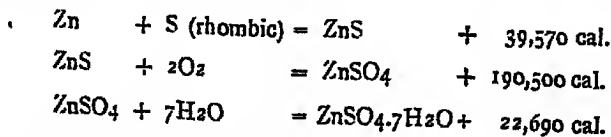
it does work, and heat is taken up, while on the other hand when a gas disappears heat is given out

Heat of endothermic compounds. Many substances are endothermic and thus evolve a great amount of heat on decomposition. Now if the affinity and the heat of formation were absolutely co-related, and thus if the heat of formation were to be taken as a direct measure of chemical affinity, there should be less than no affinity between the elements of such a compound and thus there is no force necessary to hold them together. Yet many endothermic bodies like carbon disulphide and acetylene are considered as fairly stable bodies under normal conditions.

Principles of Thermo-Chemistry.

In interpreting the results of heat energy measurements and calculating the heat of other reactions from the data collected in the above way, some general theorems are of constant application. In these reactions the chief point that is to be constantly before our eye is the final and the initial amounts of energy liberated or absorbed. Often a parallel is drawn between the potential energy of bodies and the chemical energy which one substance has for another. Thus two elements may be regarded as each possessing a certain quantity of chemical energy. When they unite, a certain portion of this is given off as heat or electrical or light energy.

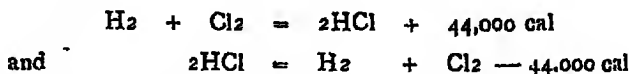
Still the compound so formed does possess the ability to unite with other elements and also compounds, and at the same time liberating an additional quantity of energy. This can be seen thus —



(1) The heat of formation of a substance is equal to its heat of decomposition. The amount of heat which

is required to decompose a compound into its constituents is exactly equal to that which was evolved when the compound was formed from the constituents. (*Law of Lavoisier and Laplace*).

Thus .



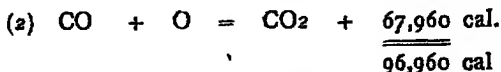
Thus the same two components, under the same physical and chemical conditions, evolve or absorb, to form the same compound in the very same manner, the same number of calories. And the sensible heat evolved in a combination (reaction) is the measure of the work done, chemical as well as physical. Save in the case of rather simple substances it is not possible to determine the heat of formation directly. Generally however it is possible only to get a rough idea about it, on the principle that it is equal to the heat of decomposition. This is of course a special application of the law of conservation of energy.

Constancy of the Heat Sum. the Law of Hess about the Heat of Formation. "The heat evolved in a chemical process is the same whether it takes place in one or in several stages." (*Hess*).

As early as 1840 Hess found out that the total amount of heat given off in a series of transformations depends only upon the final and the initial states of the substances and is independent of the several intermediate steps. In other words the amount of heat playing a part in the combination is the same whenever the initial and the final states are the same, whatever be the nature of the intermediate stages passed through.

Thus if we know the heat evolved when carbon is burned in oxygen to form carbon monoxide, and the heat evolved when carbon monoxide is burned to carbon dioxide, we would know at once the amount of heat which would be evolved when

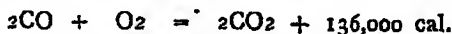
carbon is burned directly to carbon dioxide. It would be the sum of the above quantities. Thus :—



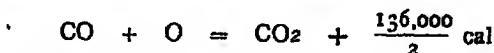
If we know the heat evolved when carbon is burned to the dioxide, and the heat evolved when the monoxide is oxidised to the dioxide, we would know the heat which would be set free when carbon was burned to the monoxide. It is the difference between the above two quantities

Examples :

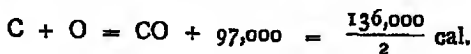
(1) Required the heat of formation of carbon monoxide, being given that .



The second equation may be represented thus .

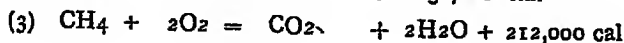
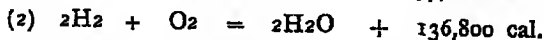
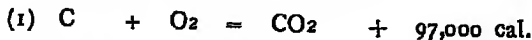


∴ The heat of formation of carbon monoxide :

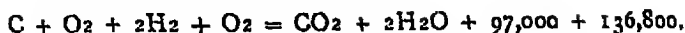


The heat of formation of carbon monoxide is 29,000 calories

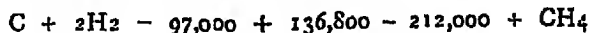
(2) Required the heat of formation of marsh gas, given that



Adding (1) and (2)



The heat of formation of methane is



Law of Thermo-neutrality. According to Hess when dilute solutions of salts are mixed neither heat is evolved nor absorbed. The law finds a ready explanation in the theory of electrolytic dissociation: Take two salts, sodium chloride NaCl and potassium bromide KBr. We know that in dilute solutions they are completely dissociated:—



When the solutions of these salts are mixed all the parts remain as ions. There is no chemical action whatsoever, every part remaining in the solution in the same condition as before. There being no chemical action, there is no reason to expect any thermal change and none results.

Some relationship between chemical reactivity and heat of reaction. It is evident from what has already been said so far that chemical changes may be divided into two classes. (1) Those that are spontaneous or proceed on themselves once they are started under the conditions of experiments, and (2) those which proceed only when forced by some external energy. Further in the light of what we have already seen so far we can also say that a chemical reaction proceeds of itself in the direction in which heat is given out, that is, spontaneous chemical changes are exothermic.

Types of heat measurements. At this stage now we are in a position to summarise the general scope of heat measurements which may be well understood by discussing a number of typical cases.

(1) **Heat of combustion.** One of the chief important determinations is the heat evolved when bodies are completely burnt and oxidised. These measurements are of great theoretical as well as technical value.

Fuel and Food are the two chief things with which we are primarily concerned in our daily life. The real value of a material as fuel depends upon its heat of combustion otherwise called its calorific value and the price paid depends upon this value.

Calorific value of fuels.

Wood (ordinary air dried)	about	4,000 cal.
Lignite	„	5,400 cal.
Bituminous coal	„	8,500 cal.
Anthracite coal	„	7,300 cal.
Coke	„	7,300 cal.

Similarly we know that one of the most important functions of food is to supply energy expended by the body. All the food that is digested ultimately undergoes oxidation in the body, and the carbon and hydrogen of the organic material is oxidised to carbon dioxide and water. The heat of the body is due to this oxidation.

The calorific value of foodstuffs

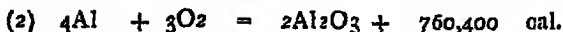
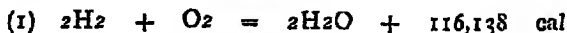
Carbohydrates	about	4,000 cal.
Fats	„	9,000 cal.
Proteins	„	4,000 cal.

(2) **Heat of formation.** This is a subject matter already fully discussed in previous articles.

(3) **Heat of solution.** When a substance dissolves in water there is always a change of temperature of the water. It may get warm or even cool down also. This change is the expression of the algebraic sum of a number of different effects. Thus a solid when dissolved first goes in a sense, in the state of a liquid and an effect something like the heat of fusion, is the result. There is also a change in the volume involving mechanical work. Similarly there may be ionization or hydrate formation etc. all involving heat change which may be either positive or negative.

(4) **Reversible reaction.** It is a well known fact that a rise of ten degrees of temperature doubles the speed of a reaction and thus an exothermic reaction should always complete itself. But such a thing is not an absolute fact because a good many reactions proceed for a short time further and further and then come to a dead stop, atleast apparently. The only explanation for such a phenomenon is that the product of the reaction must be unstable, atleast above a certain temperature, and the reverse endothermic reaction must be simultaneously taking place. In short an equilibrium is the result and the heat change in one reaction is just balanced by that in the other.

Limits of temperature in combustion. Many a time we can not reach a temperature which atleast from the thermochemical equation must positively be reached. The reason for such unexpected failure is in the secondary reactions that are taking place almost immediately the reaction is started. Thus .



make us believe that in the first equation we should get 2,400°C and in the second 4000°C should be reached. We find that the first does not happen while the second is almost a success. In the case of water formation steam is unstable and begins to decompose thus :



with considerable absorption of heat. With aluminium the product of combustion (Al_2O_3) is very stable, and hence non-absorption of heat. Thus a determining factor for the maximum temperature that can be secured by a given set of reacting substances is not only the heat of reaction which is to be accounted for but also stability of the reaction products at the high temperatures. In short reversibility or non-reversibility of the reaction would be the controlling factor. The setting in of a reverse reaction without exception puts a limit upon the rise of temperature which can be attained during the reaction.

Appendix A.

METALS.

Introduction.—Every student of elementary chemistry knows that this branch of chemistry (Inorganic) is divided into two classes. (1) Metals and (2) Non-metals. The division is not really a definite and a complete one, as there are certain elements which, so to say, form a kind of a bridge or a connecting link and as such, present no distinctive properties of either class. These on the other hand possess properties from both the classes. For this reason they are called *Metalloids* which are like hybrids in animals.

Historical.—Metals (a few of them) were the first of the elementary substances that were either found native or isolated from their salts or ores. Metals are known to people since a very remote date. The Chinese (1,800 B. C.) were adepts in smelting of minerals, so also the Egyptians (2,000 B. C.) knew how to prepare various metals and alloys. In the days of the Greeks as many as seven metals : gold, silver, mercury, copper, iron, lead and tin were known. The Indians were acquainted with a good many metals a long time before all these and the Chinese and the Egyptians got the art from the Indians. References to gold and iron are to be found in the Vedic literature.

Nomenclature.—The term metal is used as a class name from the original meaning of the word, which meant —a Mine— (anything that is searched after). Then it was applied to anything found in the mines, *e. g.* the metals.

The term 'metal' is not quite an exactly appropriate one because all the qualities that are attributed to this class of substances are not to be always found associated with this term. Here the term *base forming elements* is preferred in chemical phraseology as the hydroxides of these elements, atleast those of the lower valence are bases. But the best term

of all will be "the elements that form Cations"—simple—because when the compounds of metals are dissolved in water ionization of the salts takes place in such a way, that the metals become cations.

Occurrence—A number of metals are found in nature

I. In the uncombined or elementary condition, and in this case are said to be occurring *native*, *e. g.* gold, platinum, copper, bismuth etc. In short those that stand low in the electromotive-series

II. As a rule the metals are found combined with acid forming elements in the form of Oxides, Hydroxides and Salts of the various acids.

(1) Oxides—Iron, manganese, tin, zinc, copper and aluminium occur as oxides

(2) Salts—The most abundant salts of the various acids are the Silicates, Carbonates, Sulphides, Sulphates, and Chlorides.

(a) The natural silicates are very numerous but are seldom used for the preparation of metals. Many of them are employed for other commercial purposes

(b) From the carbonates we obtain, iron, lead, zinc and copper. Several other metals such as manganese, magnesium, barium, strontium and calcium all occur in various quarters.

(c) From the sulphides are obtained nickel, cobalt, antimony, lead, cadmium, zinc, and copper.

(d) Metals which occurs as sulphates are those whose sulphates are not freely soluble, *e. g.* lead, barium, strontium and calcium.

(e) Compounds of metals with the halogens—*Chlorides*—are not so numerous. Silver chloride AgCl furnishes a limited amount of silver. Sodium and potassium chlorides are found in the salt-beds

All such natural substances whether they contain a metal or not are called Minerals.

Those minerals which are of value for the extraction of useful substances or find application in their manufacture are called Ores. Most of these ores contain metals

Metallurgy—Extraction of metals from the ores. The art of extracting metals from their ores is called metallurgy

The metallurgy of each metal presents an individual problem depending upon :

- (1) the chemical character of the metal, ..
- (2) the nature of the ore available for its production and
- (3) its physical properties—melting point etc.

The problem is partly a physical one and partly a chemical one. In order to obtain the metal in the form of large masses and in a state approaching purity it is usually necessary to prepare it at a temperature which is above its melting point and then draw it off from the furnace in the liquid state. It is also desirable that any earthy impurity (Matrix) entering the furnace along with the ore should be converted into a liquid (Slag) which can be easily removed. To secure this end, materials are mixed with the ore, which will react with its impurities and form a liquid. The materials so added are called Fluxes, while the liquid thus produced is called the Slag. The latter usually consists of a mixture of silicates and closely resembles glass in character. The slag also acts as a liquid medium in which the small drops of the melted metal can run together into large masses and it also forms a covering over the collected material, thus protecting it from oxidation :

Ore (Metal + Matrix) + Flux = Metal + Slag

While the details in each case vary considerably, there are a few definite principles employed in metallurgy which cover the great majority of cases. Some of these are the following :

1. Reduction of the oxide.

(1) Natural oxides

(a) Reduction by carbon.

When the natural oxides are heated with carbon they are nearly all reduced



The carbon is oxidised to the dioxide or to the monoxide according to the temperature which is necessary to be employed

(b) Reduction by Aluminium.

Some oxides are not reducible by carbon in ordinary furnaces, such oxides are of Calcium, Strontium, Barium, Magnesium and Aluminium and members of the Chromium group. At the temperature of the electric furnace, even these may be reduced but here the metal combines with the excess of the carbon to form a carbide, and so it is not obtained in the pure metallic state. In such cases aluminium may sometimes be used in place of carbon to advantage.



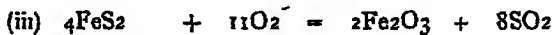
This method is come into use as a result of cheap production of aluminium and is known as Goldschmidt Process. This process has received the name "Alumino-thermy," on account of the great amount of heat liberated. This is also often called Thermite Process.

(c) Reduction by hydrogen. In the laboratory the oxides of the less active metals are reduced frequently by a stream of hydrogen.

(2) The oxides may be prepared :

As an intermediate step towards getting the free metal, first the oxides are prepared. The Carbonates, Hydroxides, and

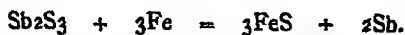
Sulphides can be changed to oxides by mere roasting—Heating—the ore with free access of air.



These oxides are then reduced according to the individual nature of the oxide.

II Reduction of the sulphides by a metal.

Just as oxygen may be removed from an oxide by a metal (aluminium) so sulphur may sometimes be removed from a sulphide by the same metal or by iron, cf. Sb or Pb :—



III Reduction of the chlorides or fluorides

The halides of the metals can be decomposed by heating them with metallic sodium : Cf. Mg and Al.



This method was formerly employed in the manufacture of magnesium and aluminium.

IV. Electrical methods.

Electrical energy is used in metallurgy for two distinct purposes. (1) Heating and the rest is done by other reagents employed—carbon—and (2) electricity is employed for bringing about the decomposition of the compound from which the metal is liberated without the assistance of a chemical reducing agent. Such processes are electrolytic in character and always take place in a liquid medium.

(1) When the metal to be produced has no action upon water the electrolysis may be conducted in an aqueous solution

The metal is then deposited directly in the solid form and at ordinary temperatures, and there is no consumption of energy in maintaining the temperature

(2) When the metal acts upon water some suitable salt of the metal is melted and the resulting electrolyte is subjected to electrolysis. Almost any melted salt would serve but many are decomposed by heat or melt only at a temperature too high to be economical. In practical work the chlorides are usually employed

Properties of the Metals

(1) Physical :

(1) Metals as a rule are solids at the ordinary temperature except Mercury.

r (2) They are usually high in specific gravity

Metals whose specific gravity is below 5 are called the Light metals, and the others Heavy metals

(3) When in bulk the metals reflect light from polished or freshly cut surfaces, and this is called the Metallic lustre. Most of the metals when very finely powdered are black except magnesium and aluminium which have shining appearance.

(4) In compact masses the metals are usually silvery white in colour. Gold and copper, which are yellow and red respectively are conspicuous exceptions

(5) The metals when they are fused and allowed to cool slowly then they crystallize and generally the crystals belong to the regular system except in case of those metals that are more non-metallic, who present a hexagonal system, *c. g.*, Sb, Bi, etc.

(6) Metals may also occur in allotropic forms, crystalline or amorphous. In certain cases the same metal may possess various specific gravities according as it has been rolled, hammered or molten. Allotropy also includes passive form of certain metals.

- (7) Usually the metals volatilize at only high temperatures.
- (8) They are good conductors of heat and electricity which they conduct without getting decomposed and hence are called conductors of the **First Class**, in distinction to the electrolytic conductors (solutions) which are conductors of the **Second Class**
- (9) Metals are **malleable**—beaten into thin sheets without loss of continuity.
- (10) Metals are **ductile**—drawn into thin wires.
- (11) They are more or less **tenacious**
- (12) The molecules of the metals are **monoatomic**

(ii) **Chemical:**

(1) Heated in air they form oxides which are base forming ones or basic ones. Again the air acts upon metals through its oxygen and also through the vapours of water and the carbonic acid gas it contains, giving rise to the formation of basic carbonates. In the case of zinc, copper and lead, these carbonates act as protecting layers and prevent further oxidation. But in the case of iron the carbonate is further decomposed and the hydroxide is formed, which being porous allows the oxidation to go on.

(2) At ordinary temperatures dry oxygen acts on potassium only. At high temperatures it acts on all the metals except gold, silver and platinum which are never acted upon. The combination may take place with evolution of heat and light e.g. magnesium, zinc or even iron wire previously heated.

(3) They generally form no compounds with hydrogen or form unstable compounds—usually non-volatile.

(4) All the metals are attacked by chlorine at different temperatures, (by dry chlorine, or by chlorine in solution). There may be incandescence (sb, cu, ..) The reactions are about the same with bromine and iodine. Halogen compounds of the typical metals are little if at all hydrolysed by water, i. e. they are fairly stable towards water.

(5) Sulphur has no action at ordinary temperatures, but at high temperatures it reacts upon metals forming sulphides, except in the case of aluminium, gold and platinum—There may be production of heat and light.

(6) Metals are easily acted upon by mineral acids giving out hydrogen

(7) Metals in solutions of their salts form cations.

The electro-positive character (and also the electro-negative character) is most pronounced for univalent elements (e.g. the alkali-metals and the halogens). But polyvalent elements may show great affinity for electricity, e.g., aluminium. On the other hand univalent elements are mostly strongly basic or acidic, and the oxides of the polyvalent elements are often both weakly basic and weakly acidic (e.g., aluminium). When the same element forms both basic or acidic oxides the higher oxides, i. e., those containing higher proportions of oxygen are most acidic.

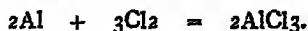
1. Preparation of Salts: General principles.

Preparation of the compounds of metals. A great many methods are employed in the preparation of the compounds of the metals. These compounds which include oxides, hydroxides and salts are very numerous, and each has its own peculiarities which must be taken into account in devising means for preparing it. In many cases some rather unusual methods are employed, (1) owing to the character of the minerals available in nature, or (2) to the accumulation of a cheap by-product in some other industry. Naturally the methods employed on a small scale in the laboratory are likely to differ from those used in industries, where economy is the first requirement. There are however some general principles which underlie the great majority of these methods and these are:—

(1) Direct union of two elements:

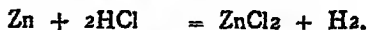
Very many binary compounds may be prepared by heating the metal with the appropriate non-metal. Among these are

Oxides, Sulphides, and Halides. The product of course is anhydrous rather than a hydrated compound. This method finds wide application when anhydrous compounds are wanted.

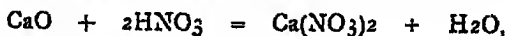


(2) Treatment of a metal, or its oxide, or hydroxide with an acid.

- (a) In the laboratory generally metals are used for preparation of salts as these are generally to be had in a degree of purity.

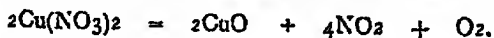


- (b) In the industries either the oxides or hydroxides are usually employed since these are usually found in nature as such or are of easy preparation.

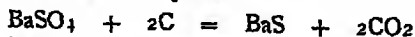


(3) Decomposition of compounds.

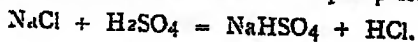
- (a) Mere heating of compounds many a time leads to the formation of simpler ones. These compounds are, Nitrates, Carbonates and Hydroxides.



- (b) Many compounds when they are heated with a reducing agent (carbon) get reduced and form simpler compounds, viz., various salts of oxygen acids are reduced by Carbon.



(4) Displacement of a volatile acid.—When a non-volatile acid acts upon a volatile acid, the latter is displaced in accordance with the general principles of equilibrium—provided the volatile acid is sparingly soluble in the liquid present.



(3) **Methods based upon precipitation.**—The formation of a precipitate when two electrolytes are brought together in solution takes place in accordance with the principles of ionic equilibrium.

In general it may be stated that :—

(a) When two salts or a strong acid and a salt are brought together in solution, double decomposition takes place with the formation of a precipitate if the union of a pair of ions produces an insoluble salt

(b) When a salt is treated with a weak acid, no precipitate is formed even though double decomposition would result in the formation of an insoluble salt.

(c) Salts of strong acids such as sulphates and chlorides, when insoluble in water are also insoluble in dilute acids

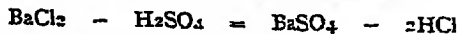
(d) Salts of weak acids such as carbonates, sulphites, and sulphides though insoluble in water are soluble in stronger acids

(A) **Double decomposition between two salts**—If barium chloride BaCl_2 and copper sulphate CuSO_4 are brought together in solution then all the salts represented in the equation would result.

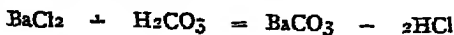


Each of these would be largely ionized and in equilibrium with its constituent ions. Among these equilibria that where the solubility product is reached is thrown down and hence appears as a precipitate.

(B) **Double decomposition between a salt and a strong acid.** With strong acids (freely ionized as the salts are) the case is quite similar with the one represented by two normal salts.



(C) **Double decomposition between a salt and a weak acid** When a salt of a strong acid is treated with a weak acid, the case is quite different. For example.



Barium carbonate BaCO_3 never comes down because the concentration of CO_3^{--} ions furnished by the weak carbonic acid H_2CO_3 is not sufficient to reach the solubility product

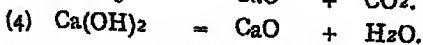
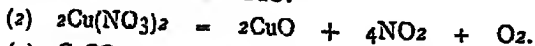
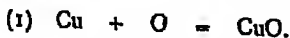
(6) **Fusion Method.**—When compounds are melted together it sometimes happens that double decomposition occurs, which would not take place if the same salts were brought together in water. In such fusion reactions one of the melted salts may be regarded as the solvent and it is to be expected that the solubility of the other in this will be different from its solubility in water. For example, barium sulphate BaSO_4 is practically insoluble in water and consequently it is not greatly affected by aqueous solution of sodium carbonate. In melted sodium carbonate Na_2CO_3 on the contrary it is readily soluble, while barium carbonate BaCO_3 is insoluble. As a consequence when it is melted together with sodium carbonate Na_2CO_3 the following double decomposition takes place.



When the mixture is cooled and warmed with water all the compounds except barium carbonate BaCO_3 dissolve and this may be filtered off and converted into any desired salt. This forms a convenient method of passing from an insoluble salt of a strong acid to a similar salt of a weak acid. Natural silicates can be decomposed in this way.

II. Preparation of compounds—(special class).

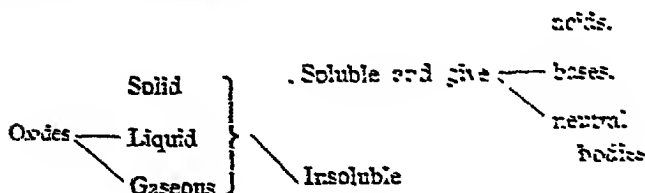
(1) **Oxides.**—The oxides can be got by (1) direct burning of the metal, (2) by heating the nitrates or the carbonates or the hydroxides.



These are usually stable except those of gold, platinum, silver and mercury which decompose when heated. They are

practically insoluble in water although the metals of the alkalis and alkaline earths give hydroxides with water H_2O . Metals like the non-metals frequently give several different oxides. In such cases as said before the lower oxides are more metallic in character, i.e., basic while the higher ones are acidic in nature. In short to summarise about oxides :

An oxide is binary compound of oxygen and some other element. Oxides are known in the case of almost every element, except a few such as fluorine. These may either be solid, liquid or gaseous.



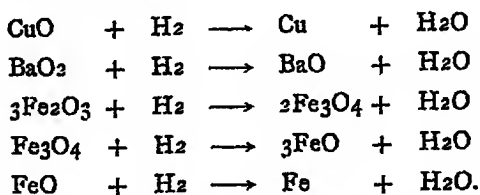
General properties of oxides.

- (1) Metallic oxides are coloured solids with no metallic lustre e.g. CuO . (dull black) ZnO (dull white).
- (2) Alkali or alkaline earth oxides are readily soluble in water with which they form hydroxides. Silver oxide Ag_2O , and lead oxide PbO are sparingly soluble. All other oxides are insoluble.
- (3) Under the action of heat oxides are :—
 - a. Totally reduced : Au , Pt , Ag , Hg .
 - b. Partially „ MnO_2 , CuO , B_2O_3 , PbO , Fe_2O_3 .
 - c. Some dissociate (i) $2CuO \rightleftharpoons Cu_2O + O$
(ii) $B_2O_3 \rightleftharpoons B_2O + O$.
 - d. Some do not change: Al , Zr , Mg , Ca , Ba , Sr .
 - e. Physically modified : fusion : SiO_2 .

- (4) Electricity decomposes a large number of melted oxides and dissolved hydroxides.

$O \longrightarrow + \text{electrode} ; m \longrightarrow - \text{pole}.$

- (5) Hydrogen has no action on alkaline and -earthly alkaline oxides ... others are totally or partially reduced :



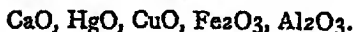
- (6) Carbon reduces a greater number of oxides than hydrogen : Cu, Fe, Pb, Zn, Sn are thus obtained in the metallic state.

- (7) Oxides are formed :—

(α) By direct oxidation of the metal.



(β) Calcination of a salt.



(γ) Double decomposition—formation of the hydroxides and then dehydration.

(2) Hydroxides.—These are formed in the case of metals of the alkali and alkaline earth metals by :

- (i) Direct union of water with the oxides. In other cases,

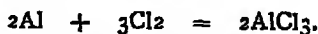
- (ii) By double decomposition when a soluble hydroxide acts upon a salt



All the hydroxides lose the elements of water and change to oxides when they are heated, except those of the alkali metals. Some hydroxides lose water by stages. All the hydroxides are insoluble more or less in water except those of the alkalis and alkaline earths.

(3) Chlorides—These salts are obtained in various ways:—

(1) Direct union of chlorine gas and the metal
e. g. FeCl_3 , SnCl_4



(ii) Action of carbon and chlorine on an oxide, of
 $2\text{Cl}_2 + \text{SiO}_2 + 2\text{C} = \text{SiCl}_4 + 2\text{CO}$,
and according to this method chromium
chloride is formed

(iii) The general methods of preparing salts.—

(a) Metal and an acid (HCl)



(b) Oxide of the metal and an acid (HCl)



(c) Hydroxide of the metal and an acid (HCl)



(d) Another salt with an acid (HCl)



(e) Double decomposition of two salts



The chlorides as a class are soluble except those of silver mercurous mercury Hg_2^+ , cuprous copper Cu_2^+ and also of lead. Most of the chlorides are also stable towards water, *i. e.*, dissolve without decomposition except those of the trivalent aluminium Al^{+++} and chromium Cr^{+++} which are hydrolysed. Also the chlorides of magnesium, calcium and zinc hydrolyse on being heated. Most of the chlorides are stable when heated except those of silver and platinum which leave the metals free on being heated. The chlorides are usually the most volatile of the salts of a given metal, hence preferred in spectrum or flame analysis.

(4) Sulphides.—They are formed by —

(1) Direct union.



(2) Solution of a salt and hydrogen sulphide H_2S .



(3) Solution of a salt and soluble sulphides.



(4) Reduction of a sulphate with carbon.



The sulphides except those of the alkali metals are but little soluble in water. The sulphides of aluminium and chromium are hydrolysed completely by water, and those of the alkaline earth metals are partially hydrolysed. When heated in air they are oxidised as a rule to SO_2 and the oxide of the metal.

(5) Sulphates —These are prepared :

(1) By the general method of preparing the salts

(2) By the oxidation of sulphides.

The sulphates are soluble in water except those of lead, barium and strontium, while calcium sulphate is meagrely

soluble When heated all sulphates except those of the alkalis, calcium, strontium, barium and lead decompose to SO_2 and O and the oxide of the metal.

(6) Nitrates—These are prepared by the usual methods for preparing soluble salts

All nitrates are (at least fairly) soluble in water. These decompose on heating generally to the oxide of the metal, NO_2 , and O, except the alkali and ammonium nitrates which change to nitrites and nitrous oxides and water respectively.

(7) Carbonates—These are prepared by the methods for making insoluble salts—double decomposition. The alkali carbonates are prepared by special methods.

All the carbonates except those of the alkali metals are insoluble and are easily decomposed on heating to CO_2 and the oxides of the metals

(8) Phosphates—Phosphates are prepared by the usual methods of preparing salts (insoluble) by double decomposition.

All the salts of phosphoric acid are insoluble except those of the alkali metals and the acid salts of alkaline earths are of varying solubility

(9) Silicates—These too like the phosphates are prepared by the usual methods for preparing salts These salts of all the metals except those of the alkalis, are insoluble in water and are also stable compounds

General behaviour of metallic compounds towards water and heat.

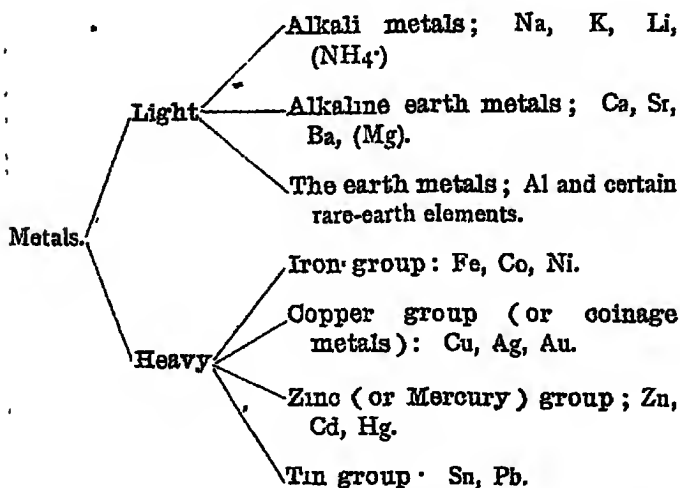
Compounds.	Effect of (good quantity) water.	Effect of heat.
1. Oxides	All oxides insoluble, except those of the alkali and alkaline earth metals	All stable, but (1) some change the stage of oxidation according to the surrounding conditions, Pb, Mn, Cr, Ba, Cu; (2) some are reduced down to metallic conditions. Hg, Ag, Au, Pt.
2. Hydroxides	All insoluble, except those of the alkaline metals and moderately the alkaline earth metals.	All change to the oxides of varying composition according to the conditions, except those of sodium and potassium which are stable, and ammonium hydroxide changes to ammonia gas and water.
3. Chlorides.	All soluble except those of Ag, Hg ₂ , Pb and Cu ₂ ⁺⁺ .	All stable but volatilize except those of silver (gold) and platinum.
4. Sulphides.	All insoluble except those of alkali metals. The sulphides of aluminium and chromium are hydrolysed by water completely, though those of the alkaline earths are partially so.	As a rule oxidised to SO ₂ and the oxide of the metal except those of the alkali and alkaline earth metals which reach only the sulphate stage.

General behaviour of metallic compounds towards water and heat.—(Contd.)

Compounds	Effect of (good quantity) water.	Effect of heat
5 Sulphates	All soluble except those of Pb, Ba, and Sr which are insoluble while CaSO_4 is meagrely so	All decompose to SO_2 , O and oxide of the metal except those of the alkalis and alkaline earths and lead
6. Nitrates.	All soluble	All decompose to the oxide of the metal, NO_2 and O except the alkali ones which decompose to nitrites, and ammonium nitrate to N_2O .
7 Carbonates.	All insoluble except those of the alkali metals.	All decompose to the oxide of the metal and carbon dioxide except those of sodium and potassium which are perfectly stable while ammonium carbonate changes to ammonia gas.
8. Phosphates.	All insoluble except those of the alkalis and the acid salt of alkaline earths that have varying solubility.	As a rule all are stable except those that have ammonium radical which escapes giving other types of phosphates.
9 Silicates.	All insoluble except those of the alkali metals.	All are stable compounds and often easily fusible

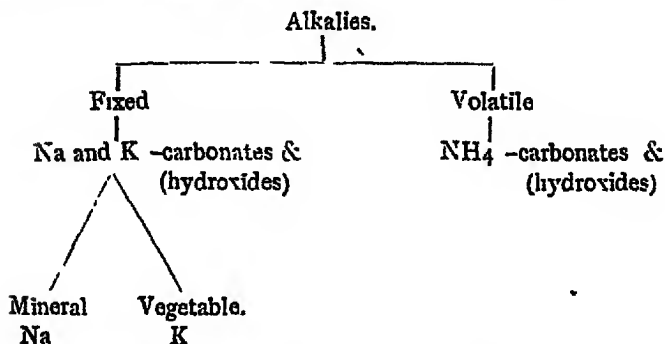
Classification of the metals.

Just as the non-metals can be arranged together in different groups according to their chemical and physical characteristics *e. g.*, the halogens, the nitrogen family etc similarly also the metals are also found to be separating themselves into different classes or groups, as they are technically called. Thus we have .

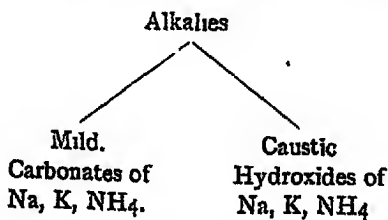


The alkali metals are often confounded with the alkalies, *i. e.*, the carbonates of these very metals, especially as the metals themselves were formerly prepared from the alkali-ash. The ash gives on analysis the carbonates of the metals (Na or K) and not the oxides as in the case of the other metals. Hence the word 'alkali' came to be fixed for the carbonates of

the metals sodium and potassium. The alkalies are themselves further classified as :—



These carbonates are all soluble in water and on hydrolysis give rise to strong alkaline reaction. Hence on account of their giving alkaline reaction which is of a base, the bases from these i. e., sodium, potassium and ammonium, also as well came to be designated by the same name : alkalies. But to avoid confusion they are separated into mild and caustic alkalies according to their intensity of action on our skin. Thus.



The word alkali is of Arabic origin meaning exactly what our word ash* designates.

* For fuller description of the term ash see appendix E

Appendix B

SILICATE (AND ALLIED) INDUSTRIES

China Clay—Although the Silicates are stable towards heat they vary considerably in their resistance to the mass-action of water and carbon dioxide and in the course of time are "Weathered." The Felspars are generally the first to be attacked, and with their decomposition the rock disintegrates. Thus the felspars of granite are transformed into soluble potassium, calcium and sodium carbonates, and silicic acid, (dissolved) which are swept into the sea or are absorbed by the soil. Aluminium silicate, which is swept down to lower levels forms the clay. In exceptional circumstances the hydrated aluminium silicate may remain undisturbed above the unweathered rock. It is then, when pure and white, known as Kaolin or China-Clay, and is valuable for the manufacture of porcelain.

Bricks.—Bricks are rectangular blocks made from ordinary clay or a mixture of clay and sand called loam baked to give them strength. The clays are the disintegration products of the older rocks, they differ very widely in composition, according to their origin. The hydrated silicate of aluminium, calcium and magnesium carbonates with iron oxide and silica &c. predominate. When heated the hydrated silicates lose their water of hydration and with it their plasticity. Once baked they do not become rehydrated in contact with water, but remain porous, hard and resistant hence their use in building. This is the chemistry of brick-making.

Mortar—Mortar is a mixture in water of slaked lime Ca(OH)_2 and sand SiO_2 . The mortar binds the bricks more firmly because it makes its way into the superficial pores of the bricks. The slaked lime at first loses water and sets to a

porous mass, then gradually by the absorption of carbon dioxide it is transformed into the carbonate. The sand assists in keeping the mortar porous and thus it ensures complete transformation of the lime. The sand itself as it is not altered, prevents the formation of large cracks, which would otherwise arise, from the shrinkage that accompanies the formation of the carbonate. The hardening does not begin until the excess of water used in making the mortar has evaporated, and hence ordinary mortar is unsuitable for use in damp places such as cellars.

Cement — Cement is made by strongly heating a mixture of lime-stone, clay and sand-stone, in the right proportion ($\text{CaO} = 50$ to 60% , $\text{SiO}_2 = 25\%$, and $\text{Al}_2\text{O}_3 = 8$ to 10%). The above ingredients are mixed together and heated until the mixture begins to sinter. The "Clinker" so obtained is ground to a fine powder and the product is called 'cement', because if it be mixed with water it sets to a hard stone like mass, even if exposed to the continued action of water and also in open air. Some natural lime-stones, containing over 20% of clay, give cements with the addition of other ingredients.

When the cement is mixed with water, it gradually sets up to a solid mass which appears to consist of a mixture of silicates of calcium and aluminium. The change proceeds throughout the whole material simultaneously, since it is not dependent on the access of any gas and not as in the case of mortar from the surface inwards. For this reason the hardening of cement occurs just as well under water as in any other locality. However the process of setting takes place best in the air, but when wholly or partially completed, the mass may be placed under water, since the compounds present, are all insoluble.

The hardening of cement is by no means understood. The general belief being that this highly basic substance by absorption of water changes to normal hydrated silicates.

Clay products

(1) **Pottery** — The crudest form of clay products, bricks, tiles, drain-tiles, &c., have little chemistry involved in their

manufacture. Naturally occurring clay is moulded into the required form and burned in a kiln but not to softening temperature. In this process the natural nearly colourless ferrous compounds in the clay are converted into the ferric compounds which give the usual red colour to these articles.

(2) **White Pottery.**—This term is applied to a variety of articles varying from the crudest porcelain to the finest china-ware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be classified as below:—

- (1) The preparation of the body of the ware.
- (2) The process of glazing.
- (3) The decoration.

(1) **The preparation of the ware.**—The materials used consist of an artificially compounded clay made from kaolin, plaster clay and pulverized feldspar. The mixture is plastic and is worked into the desired shape, by moulds or on a potter's wheel. The ware is then dried and burned until vitrified and in this form is known as "Bisque." This is usually porous and must be glazed to render it nonabsorbent.

(2) **Glaze.**—The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glass are quartz, feldspar and various metallic oxides often mixed with a little boron oxide. These materials are finely ground and mixed with water to paste. Sometimes they are first fused into a glass which is then powdered and made into paste. The bisque is dipped into the glaze paste, dried and fired until the glaze materials melt and flow evenly over the surface. The glaze must be so chosen as to resist reagents to which it is to be exposed, and it must have the same co-efficient of expansion as the body, otherwise it will check or crackle when the vessel is exposed to changes of temperatures.

However the cheapest method of glazing is to throw into the furnaces, which contain the baked earthenware, common-

salt which volatilizes and forms $\text{NaOH} + \text{HCl}$, and reacts upon the hot surface of the earthenware to form a cohering layer of sodium and aluminium silicates, that is to form an artificial felspar.

Decoration.— If the article is to be decorated, then the design may either be painted upon the body before glazing, when it is said to be underglazed, or it may be painted upon the glaze and the article fired again, the pigment melting into the glaze. In the former case the pigments used are as a rule metallic oxides, while in the latter case they are often coloured glasses.

Porcelain differs from ordinary earthenware in that after the first baking it is dipped in a milk of felspar which soaks into the pores. It is then fired again when the vessel and the felspar fuse to a homogeneous translucent mass.

Glass.

Glass is a solidified undercooled solution (mixture) of several silicates—sodium and calcium silicates—in excess of sand SiO_2 . It is a material which on cooling from the state of viscous liquid, has failed to crystallize and yet has become a rigid body. Ordinary pure quartz, when fused and cooled is an example of the simplest of the glasses. Ordinary glass as said above is a mixture of the said silicates which when melted, mix together to form a homogeneous liquid and when this is cooled, it gradually hardens to a glass.

1. Ingredients of glass.—

The ingredients ordinarily employed in glass making are sand, lime-stone and the carbonate or sulphate of sodium. When a mixture of these materials in proper proportions is heated to fusion the volatile anhydrides are driven out by the silica and the bases remain in the form of silicates. For glass of fine variety pure materials must be used while for cheap bottle-glass ordinary sand, lime-stone, and soda-ash will serve. When sodium sulphate is used in place of sodium carbonate carbon is added to reduce the sulphate to the sulphide which is

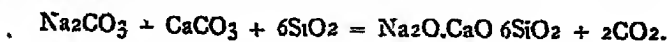
then more easily decomposed by silica. Arsenious oxide As_2O_3 is sometimes used and may act either as a reducing or as an oxidising agent depending upon the conditions. It also forms bubbles on volatilization and thus in some cases may assist in stirring the liquid and in collecting the smaller bubbles of the other gases which are always present in the melt.

The alkali silicates are soluble in water and also are amorphous and easily fusible. The calcium silicates however are insoluble, very hard to fuse and frequently crystallize. By fusing both these together, an insoluble amorphous transparent mass of moderate fusibility is obtained which is ordinary glass.

Thus in short glass is a fused mixture of silicates of sodium or potassium with one or more other silicates which are insoluble in water, such as silicate of calcium, magnesium etc. the silicates of the alkalis alone being soluble in water. In practice ground quartz or flint or clean sand mixed with potassium or sodium carbonate and the other ingredients are fritted together in an oven or a furnace by which means the silica constituting the quartz or sand enters into combination with the bases, thus forming glass.

There are many and very great varieties of glass, differing from each other in their respective compositions, qualities and uses.

The properties of glass depend primarily upon the quality of the materials and secondly upon the proportions of these materials used. By varying these two conditions it is easy to obtain grades of glass varying widely in fusibility, hardness, lustre, refractive power, etc. The usual composition of ordinary glass being $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$.



II. Varieties of glass.—

(a) Soda Glass.—(Window). It is a soda-lime-silicate. It is readily fusible and has a green tinge due to iron impurities. This is the common glass.

(b) **Potash Glass.**—(Crown, Bohemian, Jena). It is a potash-lime-silicate. It is very difficult to fuse and hence used for chemical ware

(c) **Lead Glass.**—(Flint, Cut). It is a silicate of potash and lead. It is softer, more easily fusible and highly refractive and takes on a beautiful lustre when polished. It is therefore used for optical instruments and fancy glassware

(d) **Opaque Glass**—(Milky) It is made by adding materials which remain suspended as solids in the melt or which melt along with the glass but do not mix with it. In the latter case an emulsion is formed and the turbid glass remains opaque on cooling. Fluorspar, cryolite, bone-ash, and tin oxide are used to gain the object.

III. Colour of the glass —

The colour is due to the presence of coloured metallic silicates.

Colours.		Metallic silicates
Green	Ferrous silicates
Yellow and Brown	...	Ferric "
Deep blue	. ..	Cobalt "
Ruby Red	. . .	Gold or copper in suspension.
Black	Sulphur
Yellow	Antimony.
Opalescent yellow	...	Uranium.
Violet red	...	Manganese dioxide
White	Cryolite or phosphates of calcium.

N. B.

Clay-ware differs from glass in that a natural silicate is used which does not fuse in the manufacture although it softens more or less.

Glass is toughened by plunging it into oil while hot

Note the difference between "water-glass" and "soluble glass" which are synonymous with sodium silicate and "Volcanic glass" (obsidianite) from the ordinary glass. Obsidianite is the extrusive, igneous rock which has been fused and cooled in an amorphous or nearly entirely amorphous condition. It is usually dark in colour and has a vitreous appearance and fracture. It is used in acid concentrating plants on account of its acid resisting properties.

Appendix C.

ASH.

The chemical compounds which enter into the composition of plants and animals, and their products wood, humus, fat, flesh, wool, blood, milk etc., differ in several important particulars from the common substances. These are usually more complex, that is, the molecules of such compounds contain a large number of atoms. When dried and heated strongly in air, they burn and the products of combustion are mainly gases, and are given off, but usually there remains a solid residue of incombustible material to which, whatever its composition, the name ash is given.

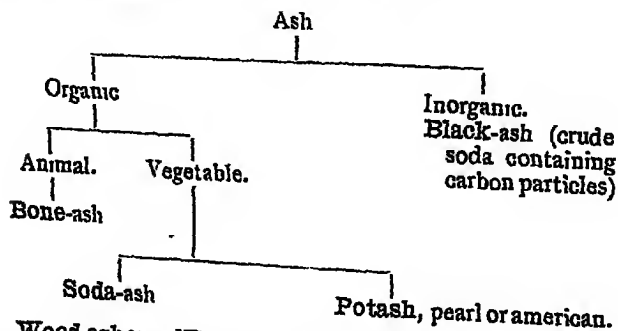
The combustible part is often called the "Organic matter" and the ash by contrast is referred to as "Inorganic" or "mineral matter". The distinction is of long standing and was originally intended to signify that, whereas the compounds which formed the combustible part were essentially products of living organisms, the ash consisted of materials which could be obtained from non-living matter. In this sense the distinction has been broken down. The constituents of the ash are (i. e. may be) products of the organisms just as much as those of the combustible matter. The two parts are however treated separately in chemical analysis, and hence the terms mentioned are convenient and are still employed for the purposes of reference.

The chemical relations of the constituents of the ash—or atleast some of them—to the compounds of which the combustible matter is made up, is in some cases well known, and in others it is very obscure. All the compounds which enter into the composition of the combustible matter contain the elements carbon and hydrogen. Oxygen is also present in a large number of them, and not a few contain one or more of the elements, nitrogen, sulphur, phosphorus and even metallic elements.

enter into the composition of some of them. When the substances are burned, the carbon, hydrogen, and sulphur combine with oxygen and form oxides. Parts of the oxygen may be derived from the substance itself, but the remainder—the larger part—is obtained from the air in which combustion takes place. Oxides of nitrogen are not formed in appreciable quantities at the temperature produced by the combustion, and practically the whole of the nitrogen is therefore liberated in the free state.

The oxides of carbon, hydrogen and sulphur are gases at the temperature of combustion and are volatilized, but in some cases small amounts are fixed by combination with basic oxides. It must not be assumed, therefore, that all the constituents pre-existed in the original substances in precisely the same form in which they are found in the ash. Milk for example contains neither carbonates, nor sulphates but the ash of milk contains both. On the other hand the calcium phosphate of which bone-ash mainly consists, is probably very similar to, if not identical with the substance present in the unburnt bones.

The quantity and composition of ash depends to a large extent upon the nature of the substance burned. Bones for instance yield nearly ten times as much ash as wood, and the ashes are composed of very different materials.



Wood-ashes When timber is felled the twigs and smaller boughs or branches are cut off and burned. Formerly this burning operation was carried out in iron pots

to facilitate the collection of ashes, and the product therefore was called "pot-ashes". These days the same process is carried on in pits dug in the ground, but the name remains.

Wood-ashes contain from 6 to 8 per cent of potassium carbonate, which can be separated almost completely from the other constituents by solution in water. The product obtained on crystallization -and which is called potash contains 50 to 60 per cent of potassium carbonate. By a further process of solution and recrystallization a still purer substance containing upwards of 90 % of potassium carbonate can be obtained. This is called 'Pearl ash' or 'American ashes.'

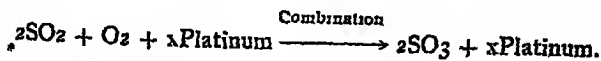
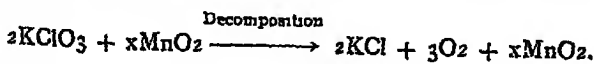
Appendix D.

CATALYSIS.

All chemical reactions have to obey certain laws, and are controlled to a great extent by the surrounding circumstances. All these factors tend to affect the rapidity of the reaction to a great extent. Especially the influence of temperature has a great effect, as it has been found that a change of ten 10° degrees doubles or halves the speed. But still surprising is the effect of the mere presence of certain materials along with the reacting substances.

Every student of chemistry knows too well the effect of manganese dioxide on the evolution of oxygen from chlorate of potash. There we find that chlorate of potash breaks up much earlier in presence of manganese dioxide than otherwise. On examining the quantities of the substances before and after the decomposition we find that manganese dioxide remains as if unaffected.

On account of this hastening of the decomposition, the phenomenon is called Catalysis [Keta-down; lyo-to loose], and the foreign substance a catalyser. Thus we may define a catalyser as a substance that increases the speed of a reaction (decomposition or formation of a compound). *e. g.*,



Similarly again we find that compounds which are unstable and hence decompose if left alone become or at the least show to be perfectly stable only in presence of certain substances *e. g.*, chloroform or hydrogen peroxide remains stable in presence of alcohol and a dilute acid respectively. These bodies may

be said to be slowing down the speed of decomposition. Whether they actually do retard the speed or some other thing happens is not our province, for the present. What we find is that the decomposition is very slow if at all it is there. Thus putting these two experimental results together we may say :

A catalyser is a substance that changes the speed of the reaction while apparently not taking part in the reaction, and without itself appearing among the final products of the reaction.

Thus a catalyser may be a positive or a negative one as it accelerates or retards the reaction. It may be a solid or a liquid or a gas or a vapour.

Theory of Catalysis. Catalyses may be likened to some incentive or awe or fear or jealousy according to the theory one adopts.

- (1) It may be likened to a lubricant. Ostwald compares its action to that of oil on the axles of a machine which move with great friction. When oiled the machine will go much faster, notwithstanding the force has not changed. The oil is not consumed, in actually increasing the speed.
- (2) It may be compared with the every day experience of children preparing their lessons more quickly in the presence of elders or when some sweets are promised in return. Here neither the parents nor the sweets are in any way taking actual and active part in the act of preparing the lessons.
- (3) It may be still more pointedly compared to the other every day experience of jealousy among two lovers when a third intruder tries to step in. Though actually he may not marry still he precipitates the marriage. Thus suppose A and B love one another and would to all probability marry after a time,

but if C comes in on the scene there is bound to be jealousy and a short friendship of C with either A or B would make both A and B hurry up and settle about their relations.

The presence of a 'foreign substance' *i. e.* which does not appear in the chemical equation proper, has always some effect. In many cases it seems to have almost no effect while in others it shows a very marked one. The substances who have marked effect on the speed or velocity are called catalytic agents. The difference is only quantitative. In theory every foreign substance acts catalytically. Catalysis is not a very well advanced phenomenon though now known for over nearly a century. It is being developed only recently simply because catalysis is a phenomenon of speed change and no conception of speed change is possible without the development of the doctrine of 'Reaction Velocity' as catalysis is change in speed of the velocity.

Catalysis is quite a common phenomenon. There is no reaction unaffected by some catalyser or other, and no substance which does not affect catalytically some reaction or other, still no general relationship can be discovered between the kind of a catalyser and the kind of reaction.

To come to the theory proper, it consists according to one school in the assumption of intermediate reactions, *viz* Let A and B be the substances which interact very slowly with formation of AB. A foreign substance, say K, when added forms KB as K and B react quicker than A and B do. But A rapidly decomposes KB in such a manner that AB and K are formed. This process can now be repeated and can continue till A or B is exhausted. K the catalyser suffers no loss.

At first sight it seems improbable that an indirect road can lead more quickly to the goal than the direct one. Yet it does happen so.

As to the second kind of catalysers -Retarding- it is not as yet certain whether these are really retarding catalysers or they simply bring about the retardation as a secondary effect, due to an inactivation of the catalyser which was present.

Auto-catalysis . Substances produced or used up during a chemical reaction act catalytically on the course of the reaction. In such a case we have auto-catalysis.

The most striking type of auto-catalysis is that a reaction in which an accelerator is formed during a naturally slow reaction *e g* Action of nitric acid on a metal like silver or copper. There the formation of the oxide of nitrogen accelerates the solution of the metal in the acid used

N. B. (1) The enzymes and organic ferments act like catalysers.

(2) Occlusion may be looked upon as a case of catalysis

Appendix E.

ALLOY.

We have often seen that two or more substances usually metals can on heating be made to mix so well, that they ultimately form one compact body. These special types of combinations are called by a distinct name: **Alloys** (a=according to; and loi=law) used formerly only with reference to legal standard of coins. Two metals are said to **alloy** when they mix together when melted, and solidify without separation.

Many elements especially metals and metalloids when melted together are mutually soluble and on being cooled the solution freezes to a solid called an alloy. On account chiefly of their consistency the alloys of mercury are called **Amalgams** (malagma=soft mass).

Preparation. The metals are melted together in a red hot crucible under a layer of carbon so as to avoid combination with oxygen. If the proportions are definite there may be got true chemical combinations attended with evolution of heat and yielding crystalline masses on cooling.

If there are no definite proportions, the alloy formed is a definite compound but dissolved in the excess of the metal.

When the alloy is subjected to slow cooling (liquidation) the mass separates out into several parts, which solidify successively at different temperatures, so giving alloys of different composition. Inversely the same separation takes place when the temperature of the solid alloy is slowly raised.

Some Important Alloys.

Alloys.	Composition.
Aluminium Bronze	Cu 90 %; Al 10 %.
Brass	Cu 70 %; Zn 30 %
Bronze	Cu 70 %; Sn 5 %; Zn 25 %
German Silver ..	Cu 60 %; Ni 20 %, Zn 20 %.
Gun metal ...	Cu 90 %; Sn 10 %.
Gold coin ...	Cu 10 %; Au 90 %
Silver coin	Cu 10 %; Ag 90 %.
Nickel coin ...	Cu 75 %; Ni 25 %.
Ferro-manganese	Fe ; Mn.
Ferro-chrome ...	Fe ; Cr.
Magnalum ...	Al ; Mg.
Solder	Pb ; Sn.
Pewter	Pb ; Sn.
Type metal ...	Pb ; Sb.
Fusible metal ...	Pb, Sn, Bi, Cd. melting at 60° and used for taking casts.

Appendix F.
UNIVERSITY EXAMINATION QUESTIONS.
 on
General Chemistry.
 for
Intermediate Science Examination
 1914.

A. N Meldrum & G B Kolhatkar.

1. State some of the important conditions which influence chemical change. Illustrate your answer by two examples of each

2 State the Law of Multiple Proportions. In the experiments on the effect of heating oxides of lead in a current of hydrogen, the following results were obtained :—

- | | | |
|----------------------------|------------------|--------------------|
| (a) 1 397 grms of litharge | gave | 1 293 grms of lead |
| (b) 2 173 " " | lead peroxide,, | 1 882 " " |
| (c) 1 712 " " | red lead " | 1 552 " " |

Show that these results are in accordance with the law of multiple proportions

3 Calculate the weight of 22.4 litres of air at 0°C and 76 cm., ignoring gases other than oxygen and nitrogen. Calculate the density, relative to air and hydrogen, of (a) acetylene, (b) chlorine, (c) water-vapour

4. State the principle laws of electrolysis. What happens when a current of electricity is passed through solutions of the following substances in series :—

Sodium chloride, sodium sulphate, copper sulphate ?

What would be the weights of the products at the different electrodes, if the action is continued till 5 grms of copper have been deposited ?

1915.

N. A. Masani & G. B. Kolhatkar.

1. Discuss fully Henry's law of the solubility of gases in liquids.

What is the effect of temperature on the solubility of (a) gases in liquids, (b) solids in liquids.

2. Explain fully what you understand by the terms, atom and molecule.

Determine the atomic weight of a metallic element from the following data :—

0.5395 grms. of the metal when converted into its chloride weighs 0.717 grms. The specific heat of the metal is 0.059.

3. Mention the important methods for the preparation of salts. Describe any two of them in detail emphasising the points which you think require attention.

* 1916.

N. A. Masani & P. V. Mehd.

1. What is meant by the term equivalent of an element ?

How is it related to atomic weight ?

1.25 grms. of a metallic element gave on dissolving in an acid 248 c.c. of hydrogen measured at normal temperature and pressure. If the specific heat of the element is 0.055 calories, what is its atomic weight ?

2. Explain fully Faraday's Laws of Electrolysis

An electric current is passed through aqueous solutions of (a) copper sulphate between copper electrodes, (b) copper sulphate between platinum electrodes, (c) sodium chloride between platinum electrodes, (d) hydrogen chloride between carbon electrodes.

Describe in detail what happens in each case. What amount of different substances is liberated when the quantity

of electricity passed through each of the solutions is one faraday ?

3. What is glass, and how is it manufactured ? Give a short account of the process.

4. An oxide of copper gave the following results —

88.8 parts of copper and 11.2 parts of oxygen by weight

What may be the formula of the oxide ? How will you proceed to obtain a sample of the oxide in the laboratory.

1917

N. A. Masani & G. B. Kolhatkar.

1. Name some gases which are combustible. Describe clearly the experiments you would perform to distinguish between any three of them.

State Dalton's Law of partial pressure.

27.3 c.c. of oxygen were measured in a dry eudiometer over mercury at 0°C and 367 mm pressure. The gas was then transferred to a vessel standing over water, and the water was brought to the same level inside and outside the vessel. What volume would the gas occupy at 27°C and 760 mm pressure ?

(Vapour pressure of water at 27°C = 26 mm.)

2. 250 c.c. of a sample of spring water required 29.8 c.c. of $\frac{N}{100}$ silver nitrate solution to completely precipitate the dissolved chlorides. Find the weight of chlorine present in combination, in 100 litres of the water. $\text{Cl} = 35.5$

1918.

N. A. Masani & G. B. Kolhatkar

1. How is the equivalent weight of an element determined ? What relation does it bear to the atomic weight ?

The sulphide of a metal gave on analysis 81.22 per cent metal and 18.78 per cent sulphur. The specific heat of the metal was 0.0303. What is its atomic weight? $S=32$.

2 (a) 112 c.c. of dry chlorine gas at N. T. P. is mixed with 385 c.c. of dry hydrogen gas at N. T. P. The gases are allowed to react. When the reaction is over, the mixture is shaken with water. What gas is left as a residue, and what volume would it occupy at 27°C and 570 mm. pressure?

(b) A compound was found on analysis to have the following composition:—

$K = 17.8$, $Ni = 13.5$, $SO_4 = 44$, and $H_2O = 24.7$ per cent. What is the formula of the compound?

$K = 39$, $Ni = 59$, $S = 32$, $O = 16$.

1919.

D. D. Kanga & G. B. Kolhatkar.

1 Explain the meaning of the term electrolysis. State the laws of the phenomenon.

A current of electricity is passed through copper sulphate solution by means of two copper plates which dip into the liquid. State and explain what may be observed. What difference would be obtained if platinum plates were used instead of copper?

2 Determine the molecular weight of ozone from the following data:—

A mixture of oxygen and ozone occupying one litre at N. T. P., weighs 1.468 grms. When treated with turpentine 50 c.c. only of the mixture are obtained. One litre of oxygen at N. T. P. weighs 1.429 grms.

or

On dissolving 1.991 grms. of a metal in dilute sulphuric acid 725.6 c.c. of hydrogen measured at 17°C and 756 mm.

pressure, were evolved The weight of one litre of hydrogen at N. T. P. is 0.09 grm The specific heat of the metal was 0.095 What is its atomic weight ?

1920

D. D. Kanga & V. B. Divatia.

1 Define and illustrate the following terms:—(1) Water of hydration, (2) Deliquescence, (3) Efflorescence, (4) Dehydration, (5) Water of constitution, and (6) Hydrolysis.

Find the number of molecules of hydration in ferrous sulphate, given that 1 grm of crystals yielded 0.84 grms of barium sulphate

2, State how the volume of a gas is related to temperature and pressure. Describe experiments in illustration of your answer.

27.3 c.c. of hydrogen were measured in a dry eudiometer over mercury at 0°C and 750 mm pressure The gas was then transferred to a vessel standing over water, and the water was brought to the same level inside and outside the vessel What volume will the gas occupy at 27°C and 761 mm. pressure ?

(Vapour pressure of water at 27°C = 26 mm)

3 Define acids, bases, and salts in terms of :—

- (a) Their properties,
- (b) Their composition, and
- (c) The ionic theory

Discuss the statement that "ordinary chemical tests are tests for ions"

4. Define and illustrate the terms.—Equivalent, atomic weight and molecular weight.

Give a clear statement of the Law of Equivalent weights

What weight of manganese dioxide must be decomposed by hydrogen chloride in order to obtain enough chlorine to combine completely with the hydrogen evolved by dissolving 10 grms of magnesium in dilute hydrochloric acid ?

1921.

D. D. Kanga & G. G. Narke.

1 (a) What weight of sodium hydroxide would be required to neutralize 100 c. c. of normal solution of sulphuric acid.?

(b) What volume of carbon dioxide measured at 15°C and 760 mm. pressure would be required to convert completely the above amount of sodium hydroxide into sodium bicarbonate ?

1922.

D. D. Kanga & R. N. Bhagvat

1. What volume of hydrogen sulphide will be evolved when 44 grms. of ferrous sulphide are treated with hydrochloric acid ?

What weight of sulphur dioxide will be obtained by burning the hydrogen sulphide formed ?

What is the nature of the reaction which takes place when sulphur dioxide and sulphuretted hydrogen gas are mixed ? Give equations.

or

How is hydrogen peroxide prepared in a pure form ? What are its properties and uses ?

How much of hydrogen peroxide solution labelled "10 vols" will be necessary if 1520 c. c. of oxygen are to be got from it at 27°C and 750 mm pressure

2. Explain the following terms, giving an example of each —(a) acid, (b) base, (c) acid salt, (d) basic salt, (e) double salt, and (f) complex salt.

What is the reaction of the solution of copper sulphate ?
How do you explain it ?

3 Henry's law states that "The solubility of a gas is proportional to the pressure." It also states that "the volume of a gas dissolved is independent of the pressure" Explain this paradox

The gases ammonia and sulphur dioxide do not obey Henry's law Show how it happens

1923

D. D Kanga & R N. Bhagvat

1 Dalton states "equal volumes of gases contain the same number of atoms at the same temperature and pressure." This statement was found to be incompatible with "Gay Lussac's law of gaseous volumes" based upon experimental facts A correct interpretation was given by Avogadro Give the correction that was introduced by him and show how it bears with the experimental facts.

2 What gas is obtained on heating ammonium nitrate ?
Give its characteristic properties.

What weight in grams of ammonium nitrate would yield on complete decomposition, 85 litres of this gas at 16°C and 748 mm. pressure ?

3 What is electrolysis ? State the laws of Faraday and explain what will happen if an electric current is passed through solutions of (a) common salt, (b) sodium sulphate, (c) copper sulphate ? What will be the quantities of products from a, b, and c if from (c) 63.6 grms. of metallic copper are liberated

1924.

A R Normand & R N. Bhagvat.

R. L. Alimohandani & V. A. Tamhane.

1 Define the equivalent weight, the molecular weight, the atomic weight of oxygen. How would you proceed to determine the above values for oxygen, taking the atom of hydrogen as your unit of weight ?

What is the usual equation representing the action of hot concentrated sulphuric acid on metallic copper ?

What volume of gas ought to be obtained by the use of 10 grms of copper, the gas being measured at 27°C and 750 mm.?

2. In experiments on the effect of heating oxides of lead in a current of hydrogen, the following results were obtained :

(a) 1.397 grms. litharge gave 1.293 grms. lead.

(b) 2.173 " lead peroxide " 1.882 " "

(c) 1.712 " red lead " 1.552 " "

Show that these results are in accordance with the law of multiple proportions.

What hypothesis accounts for this law ? Show how it does so

3. Distinguish between a metal and a non-metal. Classify copper, sulphur, carbon, phosphorus and zinc into metals and non-metals. By what experiments would you prove that your classification is correct ?

Show that the action of concentrated nitric acid on each of the above also confirms your classification.

Appendix G.

SOME IMPORTANT TERMS

Absolute Zero of temperature is -273°C at which all gases would theoretically cease to possess any volume as such.

Adsorption is the condensation of a gas or a liquid at the surface of a solid.

Acid is a substance that gives H^+ -ions in solution

- (1) Hydro-acids are those acids that have no oxygen in their molecule.
- (2) Oxy-acids are those acids that have oxygen in the molecule.

Acidity of a base is the power of a base to neutralize an acid.

Acid-strength is its reactivity at a particular concentration.

Affinity, Chemical is the unknown influences which ultimately determine the chemical reactivity.

Alkalies are the carbonates of sodium or potassium (or even of ammonium) either solid or in solution.

Alloy. Many elements especially metals and metalloids when melted together are mutually soluble and on being cooled the solution freezes to a solid then that body is called an alloy.

Amalgam is an alloy one of the constituents of which is mercury.

Amphoteric electrolyte is one whose hydroxide in solution dissociates both as an acid and as a base

Ash is the solid residue of incumbustible materials which are left behind when (organic) bodies are burnt in air.

1. Ash, black is crude sodium carbonate containing carbon particles.

2. Ash, bone is the product from the bones.
3. Ash, pearl pure recrystallized potassium carbonate.
4. Ash, pot ordinary potassium carbonate
5. Ash, soda ordinary sodium carbonate.

Association (molecular) is the loose combination between two or more molecules of the same substance, chiefly found in compounds possessing groups of marked residual affinity, $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$.

Atom is the smallest quantity of an element which can enter into chemical combination.

Avogadro's hypothesis states that equal volumes of gases or vapours under the same conditions of temperature and pressure contain an equal number of molecules.

Base is a substance that gives OH' -ions in solution.

Base-Strength is its reactivity at a particular concentration.

Basicity of an acid is the power of an acid to neutralize a base.

Bisque is unglazed white porcelain.

Boiling point—B. P.—is the temperature at which the vapour pressure of a liquid becomes equal to that of the external atmosphere.

Boyle's law states that the volume of a gas at constant temperature is inversely proportional to the pressure to which it is subjected.

Catalyser is a substance that changes the speed of the reaction along with which it is present.

Cement is a body prepared by strongly heating a mixture of lime-stone, clay and sand-stone.

Charles's law states that the volume of a gas varies directly as the temperature, the pressure remaining constant.

Clay is the natural hydrated compound of alumina and silica, resulting from the combined action of air and water upon certain felspathic rocks.

Colloid is a solid which in contrast to the crystalloid possesses no definite geometrical structure, but is either amorphous or gelatinious.

Combining Weights, law of. (Reciprocal or Equivalent). The weights of different elements which combine separately with one and the same weight of another element are either the same as or are simple multiples of, the weights of these different elements which combine with each other.

Compound is a homogeneous body composed of at least two different materials and the components of which combine in a fixed ratio, the combination is followed by a change in properties and chemical (thermal) energy.

Concentration is the percentage amount of a constituent present in a given system.

Constant is a number which, independently of the variations of certain defined external conditions, retains the same value, and is characteristic for, a definite substance, a definite physical property, or certain relations between definite physical properties.

Constant or Definite Proportions, law of. The same compound always contains the same elements combined together in the same proportion by weight.

Conservation of mass, law of. The weight of a compound is equal to the sum of the weights of the different elements forming that compound.

Critical Pressure of a gas is that pressure exerted by a gas at its critical temperature and critical volume.

Critical Temperature of a gas is the temperature, characteristic for each gas, above which liquefaction does not occur whatever the pressure.

Critical Volume of a gas is the specific volume of a gas at its critical temperature and pressure

Crystal is a body which by the operation of affinity, has assumed a symmetrical or geometrical form of a regular solid, terminated by a certain number of plane and smooth surfaces.

Crystals allotropic, are the different crystalline forms of the same chemical element.

Crystals isomorphous, are crystals of different chemical species which possess the same geometrical form, and are capable of crystallizing together as a "mixed crystal."

Crystals mixed are the bodies which, when simultaneous crystallization in the same crystal mass of distinct chemical individuals takes place, are formed.

Crystals, polymorphic are the different crystalline forms of the same chemical individual

Dalton's law of partial pressure says that the pressure of a mixture of chemically indifferent gases and vapours, is equal to the sum of the pressures which each would exert, if it alone occupied the whole space.

Decrepitation is the physical rending or flying apart of the joints of the crystalline structure of certain crystalline bodies when heated, attended with a crackling noise.

Deliquescence is absorption of moisture from the air by crystalline bodies when they are exposed to it and thereby these bodies become partly or more or less liquid in character.

Density, relative is the ratio of the mass of a given volume of a substance (solid or liquid) at 25°C to that of an equal volume of water at 4°C .

Density, vapour is the weight of a volume of a gas compared with that of an equal volume of (a) air, or (b) hydrogen.

If V D of hydrogen is taken as 1, since mol. wt.
 $H_2 = 2$ and adopting Avogadro's rule, we have

Mol Wt of a gas = $2 \times$ vapour density.

Diffusion, is the gradual penetration of one gaseous species through another

Dimorphism is the condition when a substance exhibits the property of crystallization in two forms

Dissociation, gaseous is the breaking up of a gas molecule (by increased temperature or diminished pressure into two or more simple molecules, which reunite when the original conditions are restored.

Dulong and Petat's law states that the product of the atomic weight and the specific heat of solid elements is constant (which is 6.4)

Efflorescence is that when salts which give up or lose part of their water of crystallization on exposure to air and thereby become coated with a pulverulent deposit due to this change.

Electrode is that piece of a substance which serves as a 'quay' for the departure or arrival of electricity in electrolytic conduction.

(1) **Anode** is the positive electrode, towards which move the negatively charged ions called **Anions**.

(2) **Cathode** is the negative electrode towards which move the positively charged ions called **Cations**.

Electrolysis is the act of decomposition of an electrolyte into its radicals when an electric current is passed through it.

Electrolyte is a substance which conducts electricity by means of its own molecules or their parts

Element, chemical is a body which cannot be split up into anything simpler by any means at our disposal It is also called a 'chemical primary.'

Equation, chemical is an expression used to represent a chemical reaction.

Equilibrium, chemical is the state of affair in a chemical reaction when the chemical change proceeds as fast in one direction as in the reverse.

Equivalent, chemical is the amount of an element which can combine with, or replace in combination, 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen.

Equivalent, electro-chemical is the amount of an element that is deposited from combination by one coulomb of electricity (1 ampere for 1 second).

Evaporation is the passage from the liquid to the vaporous state.

Faraday's laws :—

First law states that the mass of a substance deposited or liberated at an electrode is proportional to the quantity of electricity that has flowed through the electric cell.

Second law states that the mass of a substance deposited is proportional to the chemical equivalence of the ion.

Flux is that easily fusible material which is added to an ore to dissolve out the impurities (matrix)

Formula is the arrangement of symbols (in juxtaposition) which represents the chemical composition of a substance.

Fractional distillation is the separation of a (mixed) distillable liquid substance by distillation, by collecting the portions or fractions which pass over at varying temperatures.

Freezing point of a substance is a temperature for that substance at which both the solid and the liquid state of it may remain unchanged in contact with each other.

Gas equation, for an ideal gas volume V c. c. at pressure P per sq cm. and temperature T° Abs. is :

$$P \dot{V} = R T.$$

This is not rigidly true

Gay Lussac's law says that when a gas combines with another gas to form a compound which is also a gas then the ratio of the original combining gases and the gas formed are always in integer numbers

Glass is a solidified undercooled solution of several silicates (sodium and calcium silicates) in excess of sand.

1. Glass soluble in water glass
2. Glass, water is sodium silicate.

Graham's law says that the speed of the gases is inversely proportional to the square root of their densities.

Heat of combustion (of organic bodies) is the total amount of heat liberated by the complete combustion of a gram-molecule of a compound.

Heat of decomposition is the heat given out or absorbed when a substance is split up.

Heat of formation is the amount of heat developed (+ ve) or absorbed (- ve) in the formation of a gram molecule of exo or endo-thermic compounds respectively.

Heat of reaction is the total change of heat involved in any reaction.

Heat of solution is the amount of heat developed (+ ve) or absorbed (- ve) in the solution of a gram molecule of a substance in a large excess of the solvent.

Heat, latent, of fusion is the amount of heat necessary to transform one gram of a substance at its melting point from the solid to the liquid state.

Heat, latent, of vaporization is the amount of heat necessary to transform one gram of a liquid at its boiling point completely to the state of a gas.

Heat, specific is the amount of heat required to raise unit mass through 1°C .

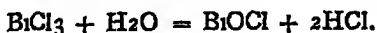
Atomic heat = specific heat \times atomic weight.

Molecular heat = " " \times molecular "

Henry's law says that the solubility of a gas is proportional to the pressure at constant temperature.

Hess, law of, states that the heat evolved in a chemical process is the same whether it takes place in one or in several stages.

Hydrolysis is the decomposition of a compound by the elements of water. *e. g.*



In the case of organic esters.



This process is often termed saponification.

Ions are the individual parts of a molecule which conduct the electric current: anions transporting negative, and cations positive electricity.

Isomorphism is that state when different substances assume the same crystalline form.

Kaolin is the ordinary clay when it is pure and white.

Lavoisier and Laplace, law of, states that the amount of heat that is required to decompose a compound into its constituents is exactly equal to that which was evolved when the compound was formed from its constituents.

Mass is the quantity of matter in a substance.

Mass action, law of, states that the rate of a chemical action in a system is proportional to the active mass present *i. e.* to the concentrations of the reacting substances.

Mass active is not the total amount of a substance taking part in a reaction but it means the concentration of the substance in gram-molecules per litre.

Matrix is the impurity usually of earthy matter that is present in an ore.

Melting point M. P. is the temperature at which the solid and the liquid phases of a substance are in equilibrium under the same vapour pressure.

Membrane, semipermeable, is a surface through which certain substances can pass freely, while the passage of others is being entirely retarded.

Mendeleeff's, law of, states that the whole of the properties of the elements, both chemical and physical, vary in a periodic fashion with their atomic weights.

Metal is an element that forms cations or that element which is base forming.

Metallurgy is the art of extraction of metals from the ores.

Minerals are natural substances found in mines. These substances may or may not contain a metal.

Mitschelrich, law of, states that substances such have analogous composition crystallize in the same shape : *e.* they are isomorphous.

Mixture is a heterogeneous body the composition of which can be varied at will and the mixing up of the components does neither result in any thermal change nor change of properties.

Molecule is the smallest amount of an element or a compound capable of individual existence.

Mortar is the mixture in water of slaked lime Ca(OH)_2 and sand SiO_2 .

Multiple proportions, law of. When the same two elements combine together to form more than one compound, the definite weights of one of the elements which combine with a constant weight of the other bear a simple ratio to one another.

Neutralization is the act of nullifying the property of an acid by a base or vice-versa.

Occlusion is the condensation of a gas or a liquid at the surface of a solid.

Ore, is a mineral which is of value for the extraction of useful substance or even finds application in their manufacture.

Oxidation is increase in the valency of an element or a radical in the positive direction or the decrease in the valency of an element or a radical in the negative direction.

Polymerisation is the state when substances have the same percentage composition but differ in their molecular weights.

Polymorphism is the state when a substance exhibits the property of crystallization in more than two forms.

Porcelain is an article made of clay & glazed with some substance that fuses at a high temperature, thus giving it a coating and at the same time binding the body of the material together in coherent mass.

Pressure, osmotic, is the pressure exerted by the particles of a solute in solution.

In very dilute solutions, osmotic pressure obeys the laws of gases with respect to the temperature and concentration of the solution.

Pressure, vapour, is the pressure exerted by the vapour of a liquid or a solid in equilibrium with the liquid or a solid at a given temperature.

Properties, additive, are the summations of the value for a given molecule calculated from the appropriate atomic constants.

Properties, colligative, are such values that they are the same for equal number of molecules of different substances.

Properties, constitutive, are the values that are not susceptible to calculations as in the case of the additive-properties.

ties, but depend upon the chemical nature and the atomic arrangement of a given molecule.

Radical is an atom or a group of atoms of the same kind or of different kinds and which acts or goes through reactions undisturbed all along and which is capable of being detached and transferred to some other.

Reaction is an action owing to which bodies modify their constitution, so as to cease being what they were and gives rise to the formation of one or more new substances.

Reduction is the decrease in the valency of an element or a radical in the positive direction or the increase in the valency of an element or a radical in the negative direction.

Reversible reaction is a reaction in which there is a state of equilibrium established due to the velocities of the direct and the reverse reactions being equal.

Salt is compound got by the neutralization of an acid and a base and eventual removal of water.

- (1) **Normal-salt** is one where in the molecule does neither contain any portion of unneutralized acid or a base still left over.
- (2) **Acid salt** is one which has some hydrogen radicals still un-neutralized in the molecule.
- (3) **Basic salt** is one which has some hydroxyl radicals of the neutralizing base still left over in the molecule.
- (4) **Complex salt** is one which yields in solution ions other than those of the salts from which it is formed.
- (5) **Double salt** is one which in solution decomposes into its constituent salts and then gives reactions for their individual ions.

Slag is the body which is formed of the mixture of solution or the flux and the matrix. It is liquid while in the furnace but solidifies to a compact mass on cooling.

Solubility of a solid in a liquid is the weight of the solid in 100 parts by weight of the liquid at a given temperature.

Solubility coefficient of a gas in a liquid is the volume of the gas at N. T. P. dissolved by the unit volume of the liquid.

Solubility product is the product of the active masses of the ions in the saturated solution of a salt

Solute is a conventional term indicative of the constituent of a solution which forms a relatively small proportion of the whole.

Solution is a homogeneous body which cannot be separated into its constituents by mechanical means, but the proportions between the constituents are, within limits variable.

Solution, ionic theory of, attributes the phenomena of electrolysis to the dissociation of the solute into ions or electrically charged particles.

Solution, pressure in the tendency on account of which ions of the metals are driven into solutions no matter whether the ions are of the same kind or of the same valency.

Solution, saturated is that solution when the solvent cannot take in any more of the solute at the same temperature.

Solvent is similar to solute a conventional term indicative of the predominating component of a solution.

(The two terms 'solvent' and 'solute' are interchangeable It is a mere question of the individual quantities.)

Sublimation is the process of converting a solid directly into its vapours without the intermediate liquid state and cooling the vapours into a solid state again

Supersaturation is a condition wherein there is presence of more of the solute than is necessary for equilibrium at a particular temperature.

Symbol is a letter (or letters) which is significant and stands for the name of an element.

Valency is that property of an element which expresses the largest number of either atoms with which the atom of a given element is known to combine directly or which determines how many atoms of another kind it can hold in combination.

Vapour density is the relative weight of a gas at the same temperature and pressure compared with hydrogen as the unit.

Vapour pressure is the pressure of the vapours of a substance (usually with reference to a liquid and especially water) exerted on the liquid and on the vessel as well.

Velocity, reaction, is the number of gram molecules of a substance transformed from one system into the other in unit of time.

Volume, specific, is the inverse of relative density : *c.* the ratio of the volume occupied by 1 grm of a substance at 25° C to that of 1 grm of water at 4°C (1 c.c.).

Water of constitution is that quantity of water that forms part and parcel of a compound and makes the nature of the compound change when it is removed from it.

Water of crystallization is that quantity (molecules) of water which is necessary for the building up of the crystals.

Water of hydration is the quantity of water necessary to form a hydrate of a substance, (either an element or a compound).

Appendix H.

I. VAPOUR PRESSURE OF WATER.

(Tension of Aqueous Vapour in mm. of Mercury.)

0°	4.6	13°	11.3	26°	25.0
1°	4.9	14°	11.9	27°	26.5
2°	5.3	15°	12.7	28°	28.1
3°	5.6	16°	13.5	29°	29.8
4°	6.1	17°	14.4	30°	31.5
5°	6.5	18°	15.4	31°	33.4
6°	6.9	19°	16.3	32°	35.4
7°	7.5	20°	17.4	33°	37.4
8°	8.0	21°	18.5	34°	39.6
9°	8.6	22°	19.7	35°	41.8
10°	9.2	23°	20.9	36°	44.1
11°	9.8	24°	22.2	37°	46.6
12°	10.5	25°	23.6	100°	760.0

II. - ELECTROMOTIVE SERIES.

(Table of order of activity of the metals.)

Each metal, when placed in a solution of a salt of one of the metals following in the list, displaces the second metal and deposits or precipitates it, in the free condition.

Potassium.	Manganese.	Tin.	Mercury.
Sodium.	Zinc.	Lead.	Silver.
Barium.	Chromium.	Hydrogen.	Palladium.
Strontium.	Cadmium.	Copper.	Platinum.
Calcium	Iron.	(Arsenic)	Gold.
Magnesium.	Cobalt.	(Antimony)	
Aluminium.	Nickel.	(Bismuth)	

III. MASSES OF 1 C. C. DRY GASES AT N. T. P.

1 c.c. of dry hydrogen at N.T.P.	weighs 0.0000199 grm.
1 c.c. of dry air at N.T.P.	weighs 0.0008203 grm.
1 c.c. of any gas at N.T.P.	weighs 0.0000449 x M. Wt.

IV. TABLE OF ATOMIC WEIGHTS.

Names of Elements	Symbol	Atomic Weight (O = 16)	Valency	Names of Elements	Symbol	Atomic Weight (O = 16)	Valency
Aluminum	Al	27.1	3	Mercury	Hg	200.6	2
Antimony	Sb	123.2	3	Molybdenum	Mo	96.0	6
Argon	Ar	39.9	0	Niobium	Nb	118.3	5
Arsenic	As	74.96	3	Nickel	Ni	58.7	2
Barium	Ba	137.37	2	Platinum	Pt	195.2	2
Bismuth	Bi	208.0	3	Radium	Ra	226.0	2
Boron	B	10.8	3	Protactinium	Pa	231.0	3
Bromine	Br	79.92	2	Ruthenium	Ru	101.1	2
Cadmium	Cd	112.40	2	Selenium	Se	79.2	4
Caesium	Cs	132.91	1	Silver	Ag	107.88	1
Calcium	Ca	40.07	2	Sodium	Na	23.0	1
Carbon	C	12.00	4	Strontium	Sr	87.63	2
Cerium	Ce	140.27	3	Tantalum	Ta	181.9	5
Chlorine	Cl	35.46	1	Tellurium	Te	127.6	2
Chromium	Cr	52.0	3	Thallium	Tl	204.0	1
Cobalt	Co	58.97	2	Thorium	Th	232.0	4
Columbium (Niobium)	Cb	93.5	5	Thulium	Tm	168.9	3
Copper	Cu	63.57	2	Tin	Sn	118.7	4
Disprosium	Dy	162.5	3	Titanium	Ti	48.1	4
Erbium	Er	167.3	3	Tungsten	W	183.9	6
Europium	Eu	152.0	3	Uranium	U	238.0	4
Fluorine	F	19.0	1	Vanadium	V	51.0	5
Gadolinium	Gd	157.3	3	Xenon	Xe	131.3	2
Gallium	Ga	69.7	3	Ytterbium	Yb	173.0	3
Germanium	Ge	72.6	4	Zinc	Zn	65.37	2
Glucinum (Beryllium)	Gl	9.1	2	Zirconium	Zr	90.6	4
Gold	Au	197.2	1				
Helium	He	4.0	0				
Holmium	Ho	164.9	3				
Hydrogen	H	1.008	1				
Iodine	I	126.9	2				
Iridium	Ir	192.2	3				
Iron	Fe	55.85	2				
Krypton	Kr	83.8	0				
Lanthanum	La	138.9	3				
Lead	Pb	207.2	2				
Lithium	Li	6.94	1				
Lutecium	Lu	175.0	3				
Magnesium	Mg	24.32	2				
Manganese	Mn	54.93	3				

Appendix I.

Explanation of how to use Logarithmic Tables.

Every student who has gone through the chapter on Logarithms must have noticed that there is a great saving of time if logarithms are used to aid the processes of solving, fractions of good man' degits, especially multiplications and divisions. A short explanation of the use of these is given below just to help the memory of the Intermediate Science students who are supposed to have gone through the chapter on logarithm in their First Year Course.

The logarithm of a number is the index of the power to which the number taken as base must be raised to equal the given number. To find the log of a vulgar fraction it must be expressed as a decimal fraction.

The logarithm of any number usually consists of two parts (1) partly integral and (2) partly fractional. The decimal fraction which is called the **Mantissa** [L. addition or increase] is found out by reference to the logarithmic table and the integral part called the **Characteristic** is obtainable by mere inspection. The characteristic may be either (1) positive (2) zero or (3) negative and which of these three, the one under question is can be settled by mere inspection of the number of which the logarithm is required. Thus —

To find the Characteristic of any number.

(1) The characteristic of a logarithm is positive if the number is greater than 1 and is one less than the number of digits before the decimal point.

(2) The characteristic of a number less than 1 is negative and is one more than the number of ciphers immediately after the decimal point.

To find the Mantissa of any number

(1) The mantissa of logarithms of all the numbers having the same significant figures are the same.

While referring to the logarithmic tables for the mantissa of a number, no notice at all must be taken of the position of the decimal point in the number under consideration, but only the significant figures be noted.

Thus 6656 is the mantissa for each of 0.0463, 0.463, 4.63, 46.3, 4630 and so on. But the characteristic will be different in all these cases

Thus —

$$\begin{aligned}\log 4630 &= 2.6656 \\ \text{" } 463 &= 1.6656 \\ \text{" } 46.3 &= 0.6656 \\ \text{" } 0.463 &= \bar{1}.6656 \\ \text{" } 0.0463 &= \bar{2}.6656\end{aligned}$$

In general it may be stated that the characteristic will be

$n - 1$ for n figures before the decimal point and n for n -th decimal place for the first significant figure

In order to find the mantissa of the logarithm of a number say of four significant figures

- (1) Look for the first two significant figures in the first column of the table.
- (2) Proceed along the row containing the above two figures and stop at the number which is just below the number which is the third figure
- (3) The number in the column headed by the fourth figure in the same row is then added to the number found in (2)
- (4) the sum is the complete mantissa

Example :—Find the log for 2567.

	0	1	2	3	4	5	6	7	8	9	1,2,3	4,5,6	7, 8, 9
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2,3,5,7,9,10	12,14,15	

$$4082 + 12 = 0.4094$$

$$\therefore \log 2567 = 0.4094$$

* Since the mantissa is always kept positive it is a common practice to write the minus sign *above* the negative characteristic so as to denote that it is the characteristic alone that and not the mantissa which is negative.

Solution of fraction involves chiefly multiplications and divisions, usually preceded by multiplications. These multiplications and divisions from the logarithmic point of view are nothing more, than either addition or subtractions of the different logs found and then their conversion by reference to the antilogarithmic table

Multiplication by Logarithms

When we have to multiply different numbers together what we have to do is first to add up the corresponding logarithms together This gives us a new logarithm. This new logarithm converted will give the number which is the actual product of the multiplication. The numbers corresponding to the new logarithm can be got by reference to the antilogarithm table

Example :--

(1) Multiply 1927×2501

Look for the figure 19 in the first column. Then proceed along the same column and the figure under 2 (2833) would be the mantissa for 192 but as we want it for 1927 we proceed further for the fourth figure in the last section of the table and there we find 15 below 7. Therefore the mantissa for 1927 would be $2833 + 15 = 2848$ and hence the log would be

$$3 \ 2848$$

Similarly for 2501 the log is $1 \ 3981$

$$3 \ 2848$$

$$1 \ 3981$$

2 6829 is the log of the product.

Now turning to the antilogarithm tables and *treating the mantissa only* exactly like the numbers that were treated for in the log table we get mantissa $6829 = 4819$. But the characteristic for the new log is 2 and hence the number which corresponds to the mantissa has to contain three figures before the decimal point and therefore it is 4819

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5
0	0000	0045	0086	0128	0170						4	9	13	17	21
1	0414	0455	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19
2	0792	0828	0864	0899	0934	0969					4	7	11	15	19
3	1139	1173	1206	1239	1271						3	7	11	14	18
4	1461	1492	1523	1553		1584	1614	1644	1673	1703	3	7	10	14	17
5	1761	1790	1818	1847	1875						3	7	10	13	16
6	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	6	9	12	15
7	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13
8	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12
9	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11
10	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11
11	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10
12	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10
13	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9
14	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9
15	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9
16	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8
17	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8
18	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8
19	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7
20	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7
21	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7
22	5051	5065	5079	5092	5105	5118	5132	5145	5159	5172	1	3	4	5	7
23	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6
24	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6
25	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6
26	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6
27	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6
28	5798	5809	5821	5832	5843	5854	5866	5877	5888	5899	1	2	3	5	6
29	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5
30	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5
31	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5
32	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5
33	6335	6345	6355	6365	6375	6385	6395	6405	6414	6425	1	2	3	4	5
34	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5
35	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5
36	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5
37	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5
38	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5
39	6902	6911	6920	6929	6938	6947	6956	6965	6974	6983	1	2	3	4	5

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
1	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
2	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
3	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
4	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
5	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
6	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
7	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
8	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
9	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
0	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
1	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
2	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
3	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
4	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
5	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
6	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
7	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
8	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
9	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	5	6
0	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
1	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
2	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
3	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
4	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
5	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
6	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	5	3	4	5	5
7	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
8	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
9	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
0	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
1	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
2	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
3	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
4	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
5	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
6	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
7	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
8	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
9	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
0	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
1	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
2	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
3	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
4	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
5	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
6	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
7	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
8	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
9	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Division by Logarithm

The process of division is almost exactly the same as multiplication except where there the different logs were added, here they are to be subtracted. Thus in division the logarithm of the divisor is subtracted from that of the dividend.

Example—Divide 3056 by 4105

$$\log 3056 = 1.4852$$

$$\begin{array}{r} \log 4105 = 0.6133 \\ \hline 0.8719 \end{array}$$

From the antilogarithm table we get

$$\log 0.8719 = 7.44 \text{ as the number}$$

But in case where the divisor is a bigger number than the dividend then a point is to be remembered when the subtraction is made. Thus suppose we have to divide

$$\begin{array}{rcl} 3805 & \text{by} & 38790 \text{ then —} \\ \log 3805 & = & 2.5804 \\ \log 38790 & = & 3.5887 \\ \hline & & 2.9917 \end{array}$$

N.B. The above examples gives us a negative characteristic in the result and leads to the principle that when subtracting the characteristic of one logarithm from that of another, the sign of the characteristic which is subtracted is to be changed and then only it is to be added to the upper number. Here thus 3 becomes $\bar{3}$, this plus the 1 borrowed in the subtraction of the mantissa which 1 is always $\bar{1}$, gives us in all $\bar{4}$ which added on to 2 give us $\bar{2}$.

The copyright of that portion of the above tables which gives the logarithms of numbers from 1000 to 2000 is the property of Messrs Macmillan and Company, Limited

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